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Effects of Coal-ash Leachate on Ground Water Quality

Tennessee Valley Authority
Chattanooga

Prepared for

Industrial Environmental Research Lab.
Research Triangle Park, NC

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16. ABSTRACT The report gives results of research to: (1) develop methodology for the field-collection of coal-ash leachate; (2) chemically characterize ash leachates from power plants using different coal sources; (3) determine the characteristics of the hydrogeochemical environment in which the leachate occurs; and (4) determine the attenuation of coal-ash leachate by various soil types. Groundwater monitoring wells were installed around ash ponds at two TVA plants. Continuous soil-core samples were collected and analyzed periodically. Ash leachate was percolated through different clays and soils to study attenuation rates. Results include indications that: (1) coal-ash leachate is highly variable, but characteristically high in dissolved solids, B, Fe, Ca, Al, and SO4; ash leachate is acidic, with measured pH as low as 2; (2) the coal sources associated with the study produced ash leachate with similar characteristics; (3) an inert-gas lift pump was effective in collecting anoxic groundwater samples while minimizing oxidation; (4) differences were found in the characteristics of leachate samples obtained by extracting the interstitial soil water and samples collected from the monitoring wells; interstitial water samples contained higher concentrations of metals and were more acidic than well samples; and (5) the flux of metals in the ash pond leachate was negligible compared to ash pond surface overflow.

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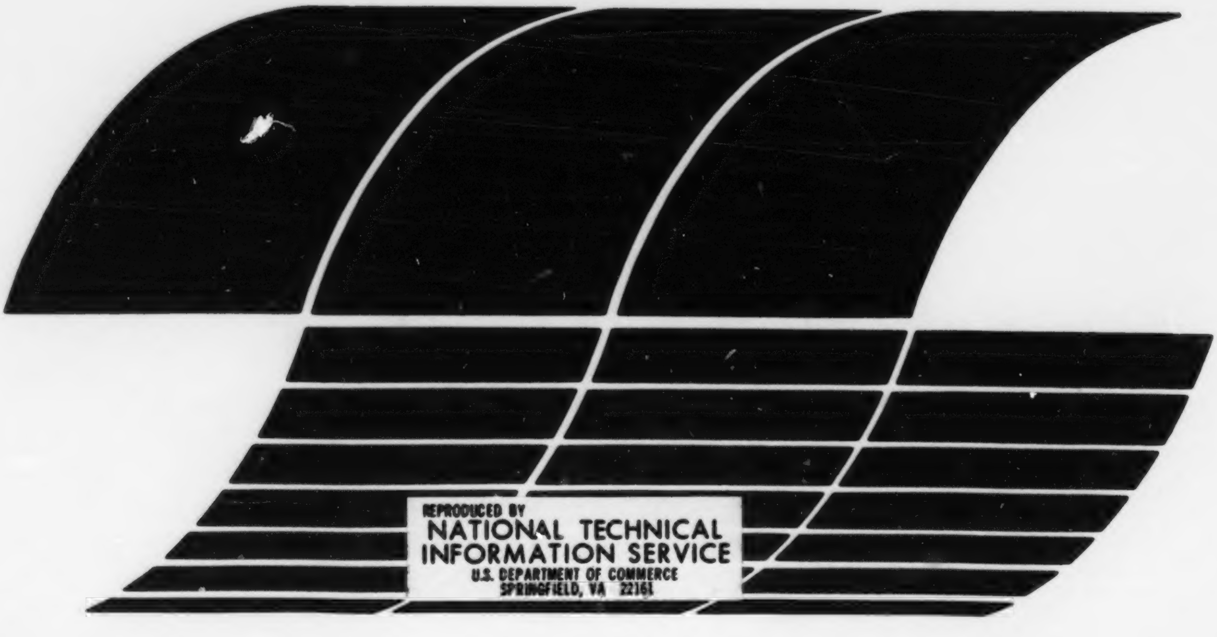

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March 1980

Effects of Coal-ash Leachate on Ground Water Quality

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ABSTRACT

The four objectives of this research are: (1) to develop a methodology for the field collection of coal-ash leachate; (2) chemically characterize ash leachates from fossil-fueled power plants using different coal sources; (3) determine the characteristics of the hydrogeochemical environment in which the leachate occurs; and (4) determine the attenuation of coal-ash leachate by various soil types.

Groundwater monitoring wells were installed around the ash ponds at two TVA coal-fired steam plants. Continuous soil-core samples were collected and analyzed for physical and chemical parameters. Groundwater samples were collected and analyzed periodically. Ash leachate was percolated through different clays and soil types in the laboratory to study attenuation rates. Results indicate that:

1. Coal-ash leachate is a highly variable solution, but characteristically is high in dissolved solids, boron, iron, calcium, aluminum, and sulfate. Ash leachate can be acidic, with pH values as low as 2 measured. Ash leachate is a chemically reducing solution.

2. The different coal sources associated with this study produced ash leachate with similar characteristics.

3. The use of an inert gas lift pump proved an effective means of collecting anoxic groundwater samples while minimizing oxidation.

4. Differences were found in the characteristics of leachate samples obtained by extracting the interstitial soil water and samples collected from monitoring wells. Interstitial water samples contained higher concentrations of metals and were more acidic than well samples.

5. The flux of metals from coal-ash leachate was found negligible when compared to the mass of metals discharged by the ash pond surface overflow (even though concentrations in the ground water were highest) because the surface discharge was much greater than the groundwater flow.

This report was submitted by the Tennessee Valley Authority, Office of Natural Resources, in partial fulfillment of Energy Accomplishment Plan 80 BDO under terms of Interagency Agreement EPA-IAG-D5-E-721 with the Environmental Protection Agency. Work was completed as of November 1979.

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SECTION 1

INTRODUCTION

The increasing use of coal for power generation will result in an increasing potential for adverse environmental impacts. Realizing the importance of knowing what impacts power generating facilities may have on the environment and anticipating the forthcoming Federal regulations applying to solid waste disposal (Resource Conservation and Recovery Act, P.L. 94-580), the Tennessee Valley Authority (TVA) in conjunction with the Environmental Protection Agency (EPA) initiated a study to characterize the various effluents associated with coal-fired generating facilities. As a part of that study, entitled "Characterization of Effluents from Coal-Fired Utility Boilers," the impact of coal-ash leachate on groundwater quality at two TVA fossil-fueled power plants was investigated.

TVA's coal-fired generating system produces approximately 650 tons of coal ash for every 1000 megawatts generated. During 1977, TVA's 12 coal-fired power plants produced approximately 6.7 million tons of ash. The ash consists of various proportions of fly ash and bottom ash depending on the methods of firing and ash collection systems used at the plants. Once collected, the ash is sluiced with raw river water to nearby settling ponds. After settling, overflow from the settling pond is discharged to adjacent receiving streams in compliance with the EPA National Pollutant Discharge Elimination System permit.

Ash leachate is generated by the infiltration of ponded sluicing water into the settled ash, and its subsequent percolation through the ash where it eventually acquires the characteristics of ash leachate. The dry disposal of coal-ash, or ash ponds that are no longer inundated, such as a filled pond, can generate ash leachate with water from direct precipitation and/or rainfall runoff. Once the leachate is generated and has entered the subsurface environment below the deposited ash, its chemical characteristics can be affected by various attenuation phenomena. This report presents the results of a field and laboratory project performed to characterize coal-ash leachate and its attenuation by selected soil types at two TVA power plants. The major objectives of the project were to: (1) develop a methodology for the field collection of coal-ash leachate, (2) chemically characterize ash leachate from fossil-fueled power plants using different coal sources, (3) determine the characteristics of the hydrogeochemical environment in which the leachate occurs, and (4) determine the attenuation of coal-ash leachate by various soil types.

SECTION 2

CONCLUSIONS AND RECOMMENDATIONS

Results of the ash pond leachate investigation indicate:

1. Coal-ash leachate is a highly variable solution, but characteristically is high in dissolved solids, boron, iron, calcium, aluminum, and sulfate.

2. Several constituents in ash leachate were found to exceed EPA's criteria for drinking water. These include cadmium, chromium, iron, manganese, and lead. Dissolved solids and pH also did not meet these criterion.

3. Ash leachate can be acidic, with pH values as low as 2.0 measured. This acidity was found at two steam plants even though one generated an alkaline ash.

4. Ash leachate is a chemically reduced solution.

5. The different coal sources associated with this study produced ash leachate with similar characteristics. However, the acidic ash at one plant produced higher concentrations of metals in the leachate than the alkaline ash at another plant.

6. The use of an inert gas lift pump provides a means of collecting anoxic groundwater samples while minimizing oxidation.

7. Differences found in the characteristics of leachate samples obtained by extracting the interstitial soil water and those of samples from monitoring wells include: (a) interstitial water samples were more acidic than well samples, (b) interstitial water samples contained higher concentrations of metals than well samples and, (c) the collection of interstitial water samples by compressing soil samples is a time consuming and costly technique relative to the collection of water samples via monitoring wells. Further investigation into groundwater and leachate sampling techniques and their effects on sample integrity is needed to ensure accurate evaluations of leachate impacts.

8. Coal-ash leachate migration and/or attenuation in subsoils cannot be accurately determined by analyzing total soil samples for leachate constituents. Fractionization and analysis of specific particle sizes may be necessary to reduce the large variation associated with total soil sample analysis.

9. The mass of metals in the ash pond leachate entering adjacent surface water was found negligible when compared to the mass discharged by the ash pond surface overflow (even though concentrations in the ground water were higher) because surface flows were much larger.

10. Soils containing a large percentage of clay provide a better medium for attenuating metals from ash leachate than soils with more sand.

11. The anoxic leachate attenuation system, developed during this investigation, is a viable approach for studying leachate attenuation by soils under anoxic conditions.

12. Further work on the speciation chemistry of coal-ash leachate needs to be performed to determine if toxic metal species are present.

SECTION 3

LITERATURE REVIEW

The solubilization of ions from coal ash during the percolation of water through ash disposal areas and their potential for groundwater contamination, have long been recognized. In a study conducted during 1951 and 1952 by Merz and Snead,[1] the leaching of soluble salts and alkaline compounds from incinerator ash dumps was investigated. Their studies indicated that salts and alkaline compounds would leach from ash during the percolation of water from direct precipitation and/or groundwater movement through the ash; however, the leaching rate would be very low. The study also found that chlorides, nitrates, and sulfates were the most readily leached anions, and sodium and potassium were the most readily leached cations. Calcium and magnesium were found to leach, but very slowly. A limited number of leachate samples were also analyzed for copper, aluminum, lithium, manganese, vanadium, barium, boron, and strontium. Only boron and strontium were found in quantities above one milligram per liter.

In a much later report, Rohrman[2] discussed a comprehensive ash study which involved 12 fossil-fueled power plants. One of the major findings of this study was that all the ponded ash sluice waters contained boron and phosphorus, and data was presented showing that many of the elements in coal ash were present in the oxide form. In one of the first studies to determine the major chemical elements of coal-ash leachate, O'Connor, et al.,[3] mixed 50 grams of fly ash of different ages with 500 milliliters of demineralized water and analyzed the liquid for extracted solutes. This study indicated that the coal-ash extract could be characterized as an alkaline solution of calcium sulfate. The pH of the extracts ranged from 7.5 to 11.1, calcium ranged from 27 to 288 mg/l, and sulfate from 45 to 600 mg/l. An additional finding was that the pH of the extract decreased with increasing age of the ash, but a reason for this is unknown. As a further part of this study, coal ash was placed into columns and subjected to repeated elutions with demineralized water. In this experiment, the highest concentrations of solids were observed during the first elutions and most of the readily soluble constituents were eluted with the first three liters of elutant. Calcium and sulfate were found to be the most abundant ions in all the elutants. Between pH 10.0 and 11.5, calcium was equal to the total hardness. At a pH below 10.0, calcium accounted for approximately half the hardness, indicating the solubilization of other hardness-producing ions.

In a study by Weeter, et al.,[4] 500 grams each of fly ash and bottom ash were mixed with two liters of distilled water for 48 hours. The liquid of this mixture was then analyzed for the extracted solutes. The results of their analysis is presented in Table 1. The calcium and sulfate concentrations in fly ash samples ranged from 400 to 600 mg/l and from 1300 to 2000 mg/l, respectively, somewhat higher concentrations than those found by O'Connor, et al. However, in the O'Connor study a smaller concentration of ash was used in the mixing experiment. The concentration of solutes in a water-ash mixture has been shown by Weeter to be dependent on ash concentration. Batch mixing studies performed by Weeter indicated that the supernatant concentrations of sulfate, alkalinity, calcium, and iron increase with increasing fly ash loading, and steady-state concentrations for these constituents were found to occur within a mixing time of one hour. This indicates that the most readily soluble constituents in coal ash are loosely bound to sites on the surface of the ash particle.

TABLE 1. CHEMICAL CHARACTERISTICS OF COAL-ASH SHAKER TEST SUPERNATANT[a] (after Weeter, et al.)

Parameter	Fly ash[b]	Bottom ash[b]
Iron	0.1-1.8	0.05-0.15
Potassium	33-112	0.4-6.6
Calcium	400-600	8-135
Magnesium	1-19	0.8-7.1
Titanium	Trace	0.1
Arsenic	0.01	0.01-0.8
Boron	3-10	0.1-0.2
Aluminum	1.5-6.8	0.05-0.5
Sodium	15-90	0.8-7.8
Sulfate	1300-2000	12-60
Phosphate	0.1-0.6	0.1-0.5
Silica	3-40	1-2

[a] 500 grams of ash with 2 liters of distilled water; shaken for 48 hours.

[b] Values in mg/l.

In batch shake tests similar to those performed by Weeter, Theis and Wirth[5] mixed various weights of fly ash that were collected from different plants with one liter of distilled water and determined the equilibrium pH of the supernatant. Their experiments indicated that equilibrium pH levels were achieved with an ash concentration of 1 to 2 grams per liter. They also discovered that some ashes induced alkaline conditions in the supernatant, while others produced acidic conditions. An analysis of the supernatant for trace metals showed that the highest concentrations were present in the acidic ash mixture, indicating increased solubilization as would be expected with the depressed pH.

In addition to changes in the pH and metals concentrations, changes in the dissolved oxygen concentration resulting from the addition of fly ash, have been found. In Figures 1 and 2, from Theis,[6] it can readily be seen that after mixing fly ash with water the original dissolved oxygen concentration is depressed, and the pH either increased or decreased. The decreased dissolved oxygen concentration may be a result of oxygen depletion by a sulfite ion oxidation reaction, and may be expressed by:

$$SO_3^{-2} + 1/2\ O_2 \rightarrow SO_4^{-2}$$

The rate of this reaction is normally very slow:[7] however, the catalytic effects of metal ions in this reaction are well known, and the reaction rate may also be affected by certain organic compounds. Increases in pH are likely a result of the solubilization of calcium oxide (lime) present on the surface of the ash particles. Upon mixing with water, calcium oxide becomes hydrated as follows:

$$CaO + H_2O \rightarrow Ca(OH)_2$$

In distilled water partial dissociation of the hydrated lime would cause an increase in pH. In an actual coal ash disposal area, water mixed with ash would contain alkalinity and hardness. Under these conditions, an increase in pH would result from the establishment of the following equilibriums:

$$CaO + H_2O \rightarrow Ca(OH)_2 \quad \text{hydrated lime formation} \qquad (1)$$

$$Ca(HCO_3)_2 \rightarrow Ca^{+2} + 2HCO_3^- \qquad (2)$$

$$HCO_3^- \rightleftarrows CO_3^{-2} + H^+ \qquad (3)$$

$$CO_3^{-2} + H_2O \rightleftarrows HCO_3^- + OH^- \qquad (4)$$

Equations 3 and 4 effectuate the increase in pH by removing hydrogen ions in equation 3 and increasing hydroxide ions in equation 4. These reactions, along with others, were utilized by Chu[8] in a study to demonstrate the efficacy of lime-soda ash softening of ash pond water for closed-cycle water reuse in power plants.

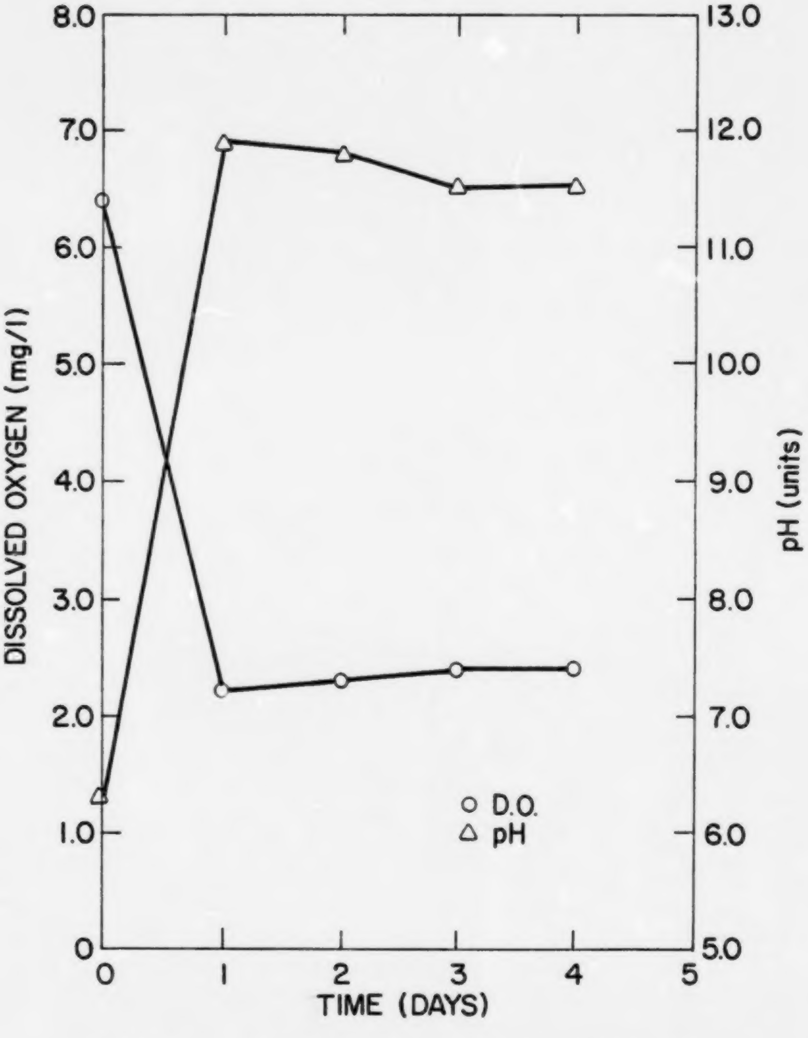

Figure 1. Effects of fly ash with lime on pH and dissolved oxygen of distilled water (after Theis).

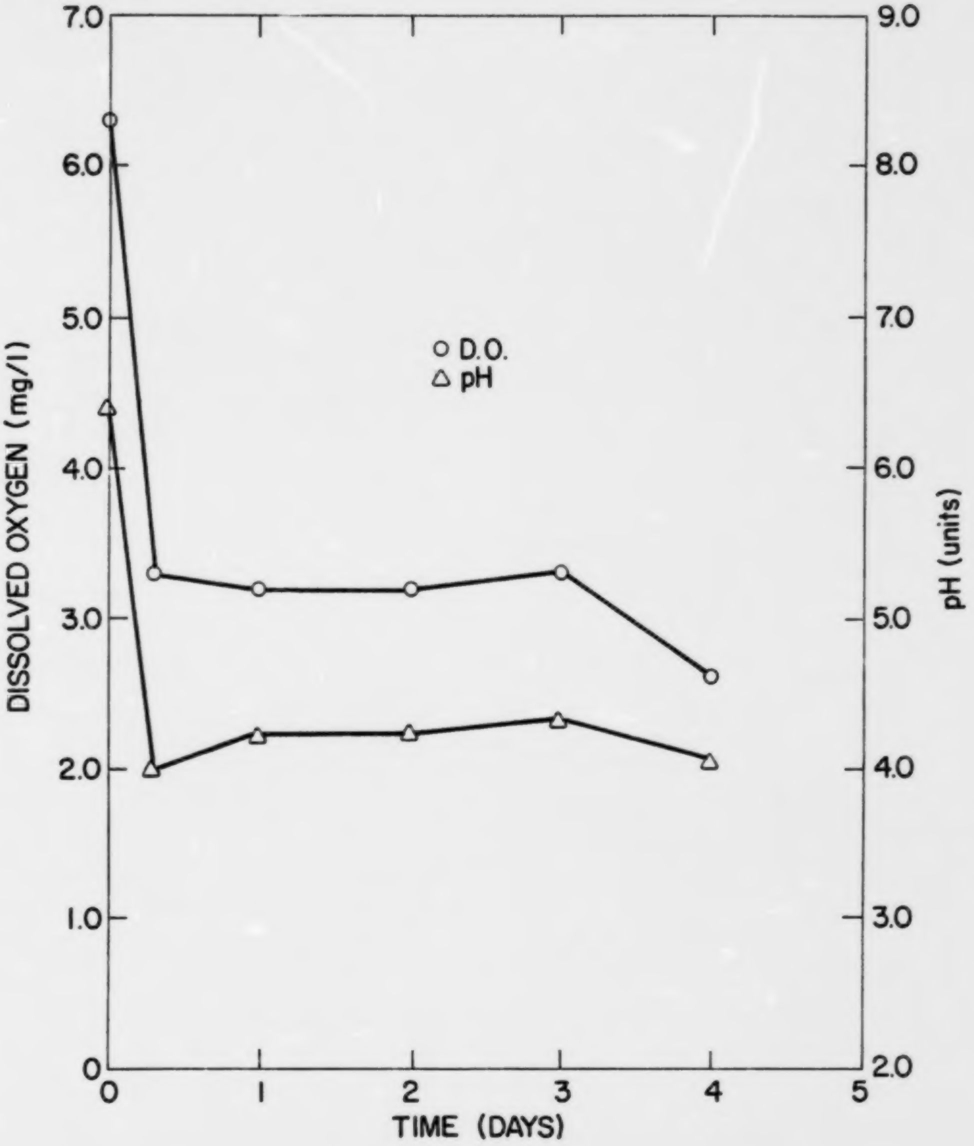

Figure 2. Effects of fly ash with lime on pH and dissolved oxygen of distilled water (after Theis).

Certain ashes may contain high concentrations of transition metal oxides, concurrent with low quantities of lime. Under these circumstances the acidic character of the transition metals, especially iron, can cause decreases in solution pH. In addition, salts of metal ions show varying degrees of acidity when dissolved in water; hydrolysis of these ions effectuates acidic conditions. For example:

$$Fe(H_2O)_5\,OH^{+2} + H_2O \rightleftarrows Fe(H_2O)_4(OH)_2^{+} + H_3O^{+} \qquad (7)$$

Decreased solution pH could present a potential water quality problem if a portion of the metals associated with coal ash were present on the surface of the ash particle where they could be easily solubilized. The sorption properties of fly ash were also investigated by Theis, and his findings indicated that surface coatings of amorphous iron, manganese, or aluminum oxides could provide a sorptive medium for trace metals.

Reed, et al.,[9] performed mixing studies using various concentrations of fly ash. From these studies he concluded that equilibrium concentrations were established within 20 minutes of contact. He also noted that the equilibrium concentrations achieved under his batch study were considerably lower than concentrations found by Burnett,[10] during a column percolation study in which fly ash from the same location was used.

In another column study performed by Brown,[11] distilled water was percolated through plastic columns filled with coal ash. Successive volumes of the percolate were then analyzed for various elements. The concentrations found in the percolate by Brown were considerably higher than concentrations found by previous investigators using batch mixing techniques. Column percolation studies tend to allow greater contact time and higher ash-to-water ratios than batch tests. These investigations indicate that column studies may be a more accurate method of predicting actual coal-ash leachate quality.

Harriger, et al.,[12] in one of the few recent studies to characterize coal-ash leachate by analyzing groundwater samples, reported highly variable concentrations of calcium, sulfate, alkalinity, iron, and magnesium in groundwater samples collected in an ash disposal area, and much higher values overall as compared to samples collected away from the ash disposal area. Some of their values are presented in Table 2 for comparison with values obtained in laboratory studies using batch and column techniques.

TABLE 2. COMPARISON OF COAL ASH LEACHATE OBTAINED BY DIFFERENT TECHNIQUES

Parameter	Mixed batch extraction[a]	Column elution extraction[b]	Leachate well sample[c]
Calcium, mg/l	20-280	490	91-660
Sulfate, mg/l	18-740	39,000	345-4000
Alkalinity, mg/l as $CaCO_3$	42-190	390	56,000-985,500
Iron, mg/l	0.03-0.1	0.1	0.04-10.4
Magnesium, mg/l	1-19	80	2.6-16.8
Arsenic, mg/l	0.01	0.13	0.01-0.19

[a] Weeter (see references).

[b] Brown (see references).

[c] Harriger (see references).

SECTION 4

DESCRIPTION OF ASH DISPOSAL AREAS

This section describes the coal-ash disposal areas at plants J and L, and provides some detailed information regarding coal use and ash generation. In addition, the geological stratigraphy beneath both disposal areas is described.

PLANT J

Plant J is a coal-fired power generating facility located on a peninsula formed by two reaches of the Clinch and Emory Rivers in eastern Tennessee. The facility was put into full operation in December 1955, and has a rated power generating capacity of 1700 megawatts. The plant utilizes coal produced in eastern Tennessee and eastern Kentucky which has an average of 2.0 percent sulfur and 19 percent ash. During 1972 the plant consumed 3.9 million metric tons of coal, and generated 711,682 metric tons of ash. The ash consisted of 560,002 metric tons of fly ash, and 151,680 metric tons of furnace bottom ash. The fly ash is collected by mechanical collectors and electrostatic precipitators installed in series, with an overall efficiency of 98 percent. The bottom ash is collected in hoppers located at the bottom of the furnace. The ashes required 30,112 million liters of raw river water to sluice it from the collection systems at the plant to a nearby ash settling pond for disposal.

The original coal-ash disposal area at plant J (ash pond A) consisted of a 242,800 m^2 settling pond. This pond was completely filled with ash by 1972 and is no longer in use. The current disposal pond has an area of approximately 594,900 $m.^2$ The pond is situated adjacent to the Emory River (see Figure 3) with the pond retainer dike separating the pond and river. The pond overflow is discharged over a weir into a small embayment of Watts Bar Reservoir.

The thickness of the ash in plant J's disposal area ranges from 0.5 meters near the pond's overflow weir to 14 meters in the original 242,800 m^2 pond. The whole disposal area is underlain by (1) a clay-silt stratum immediately below the ash ranging in thickness from 2.4 to 6.1 meters, (2) a deeper alluvial sand stratum ranging in thickness from 1.5 to 3.6 meters, and (3) low permeability shale.[13] The thickness of the shale is not accurately known.

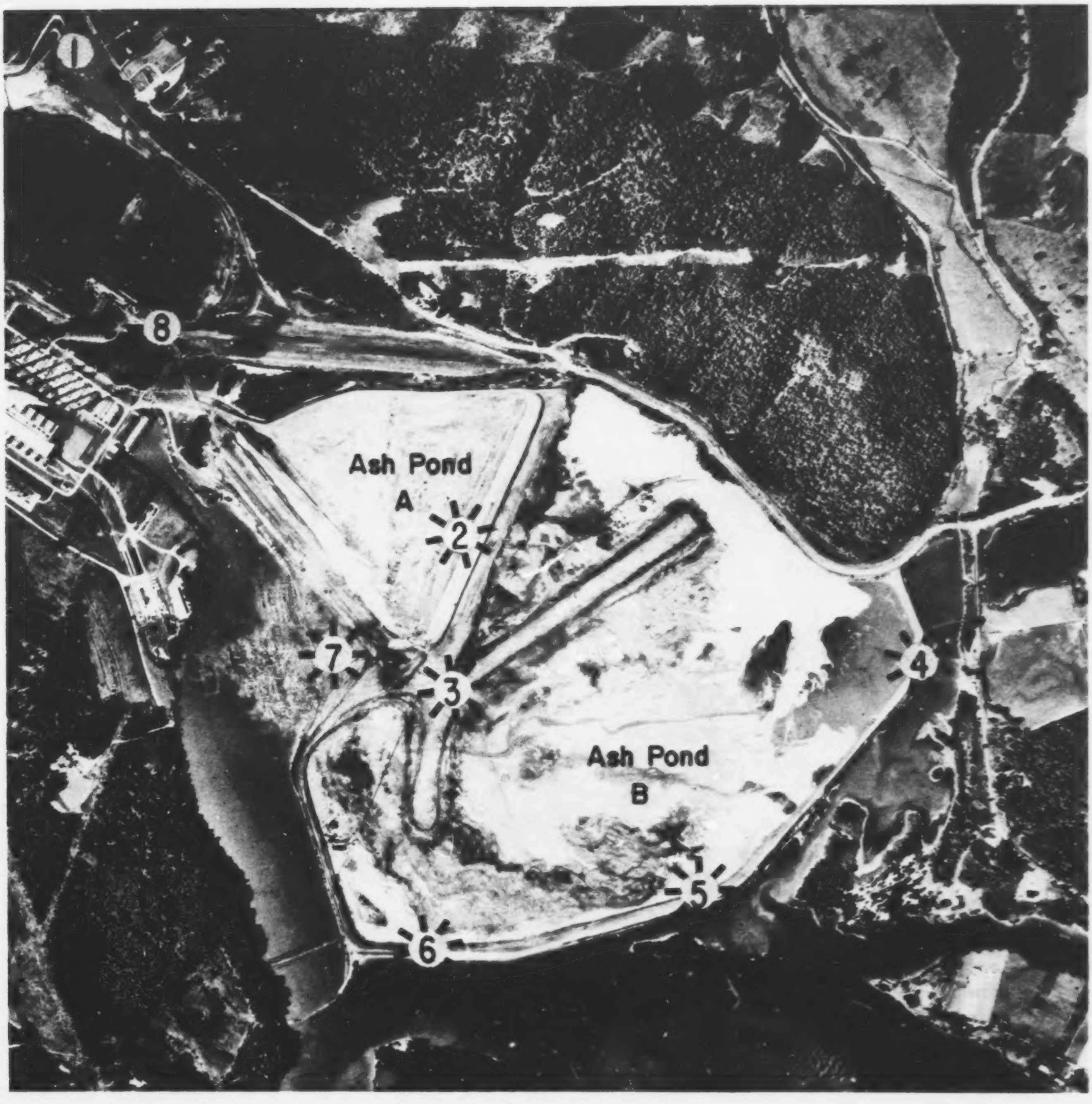
1
8
Ash Pond
A
2
7
3
4
Ash Pond
B
5
6

Figure 3. Plant J - ground water sampling well locations.

The ash pond dike itself is composed of a variety of materials with varying compositions, mostly silty clay, but deposits of ash are present. The height of the dike from the original ground surface to the top of the dike was approximately 4.5 meters.

PLANT L

Plant L began commercial operation in 1952, with three coal-fired units generating about 420 megawatts. By 1975, five additional units had been added bringing the total full load generating capacity of the plant to about 1965 megawatts. The facility is located on the Tennessee River in northeastern Alabama. The plant burns coal obtained from areas in western Kentucky and north Alabama which averages about 2.8 percent sulfur and 16 percent ash. During 1972, the plant consumed 3.3 million metric tons of coal and produced 432,361 metric tons of ash consisting of 107,228 metric tons of bottom ash and 325,133 metric tons of fly ash. The fly ash is collected by electrostatic precipitators or mechanical collectors and the bottom ash is collected in hoppers located at the bottom of each furnace. The volume of raw river water required to sluice the ash from the collection systems to nearby ash settling ponds during 1972 was about 27,725 million liters.

Plant L originally had two principal disposal areas (see Figure 4), ponds 1 and 2. Pond 1 is no longer active or inundated and has begun to revegetate. Currently, all the ash discharged from the plant is received by pond 2. This pond is 95 percent full and acts merely as a conduit to transport the ash to pond 3, which is the latest ash pond constructed. Some settling occurs in pond 2, but it is mostly the very coarse, heavy material. Most of the ash is settled in pond 3. The total ash disposal area, including ponds 1, 2, and 3, is approximately 1,032,000 m^2.

The thickness of the ash in plant L's ash disposal area ranges up to 11 meters in depth. The greatest ash depths occur in the older ponds 1 and 2. Underlying the ash disposal areas, there are three geological formations present:[14] (1) recent deposits of river alluvium, (2) older river terrace deposits, and (3) limestone.

The material overlying the limestone bedrock in the disposal area was deposited by the Tennessee River. There is no clear-cut delineation between the alluvium and the terrace deposits. Both are composed mostly of clay and silt with some sand and gravel mixtures. In the ash disposal area, these deposits vary in thickness from 3.8 to 9.0 meters. The underlying bedrock in the area is Ordovician age limestone several hundred feet thick. Its composition is mainly shaly limestone with interbeds of purer limestone and zones of varicolored siltstone or argillite. There are numerous cavities in the limestone resulting from its dissolution by ground water.

Pond No. 3's dike material is composed of a highly compacted clay of low permeability. The thickness of the dike from its interface with the original ground surface to the top of the dike is approximately 10 meters.

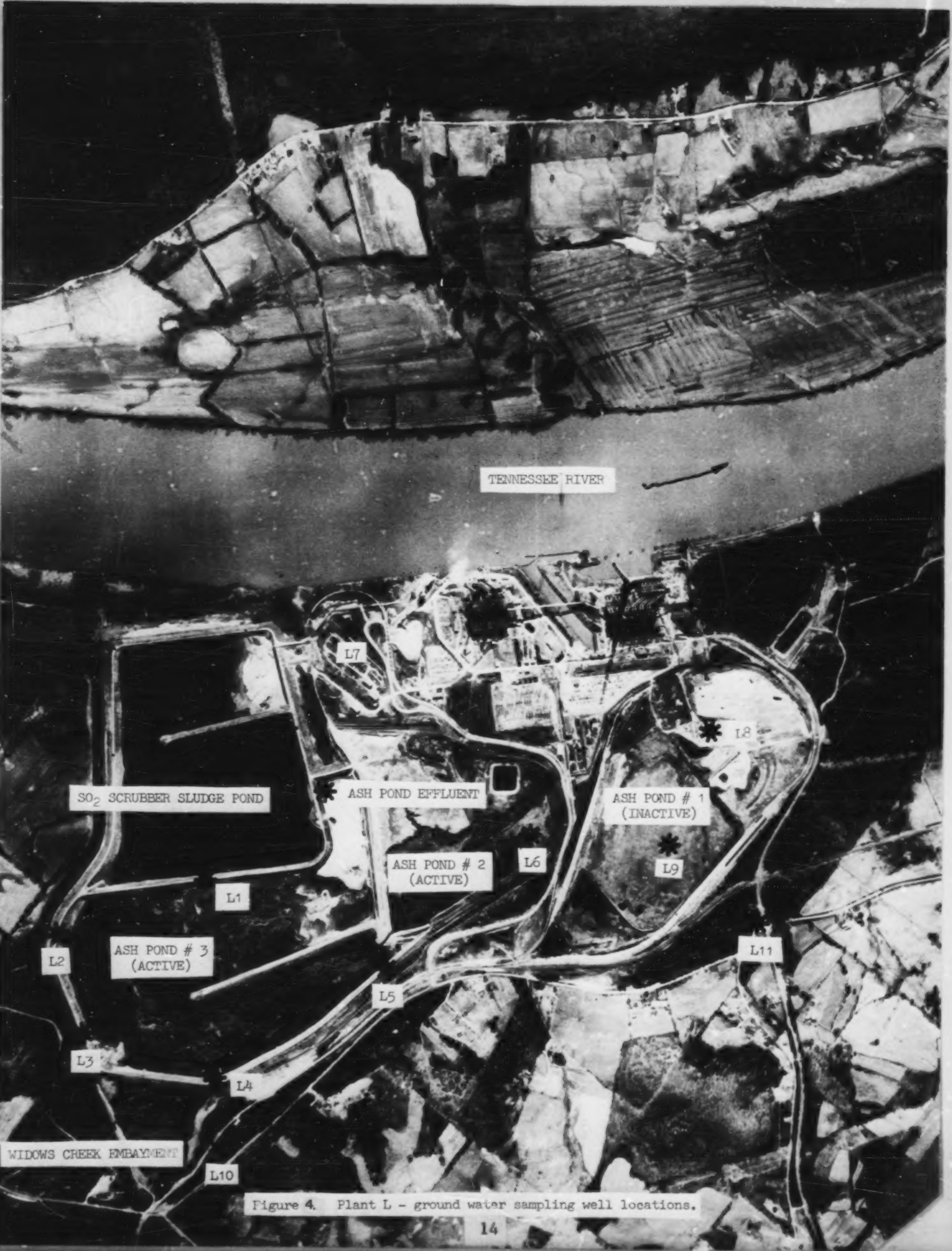
TENNESSEE RIVER
L7
L8
SO$_2$ SCRUBBER SLUDGE POND
ASH POND EFFLUENT
ASH POND # 1
(INACTIVE)
ASH POND # 2
(ACTIVE)
L6
L9
L1
ASH POND # 3
(ACTIVE)
L2
L11
L5
L3
L4
WIDOWS CREEK EMBAYMENT
L10

Figure 4. Plant L - ground water sampling well locations.

SECTION 5

METHODOLOGY

This section describes the methods and procedures used to obtain data on ash leachates, groundwater contamination, leachate migration, and leachate attenuation by soils. The project involved field investigations at two power plants with different coal sources and subsurface soil conditions, and a laboratory simulation of leachate attenuation using leachate collected at one of the power plants.

FIELD INVESTIGATION

Plant J - Groundwater Sampling Well Design and Installation

During March and April 1976, groundwater sampling wells were installed at eight locations in and around the ash disposal pond at plant J (see Figure 3). Two of the eight sampling sites (J1 and J8) are located hydraulically upgradient from the ash disposal area and function as background locations. Site J2 was located in an older section of the disposal area, which is no longer inundated and is presently used as an equipment storage area. Site J3 was located in an area of the active disposal pond that had recently been filled and was stable enough to support drilling equipment. Sites J4, J5, J6, and J7 were located on the peripheral retainer dike downgradient from the active disposal area and were spaced in such a manner as to intercept any lateral flow of ash leachate from the ash disposal area.

To install a sampling well, a "split-spoon" soil sampler with a diameter of 5.1 cm was first used to obtain a soil sample and then a hollow-stem auger having a 30.5 cm outside diameter and powered by a hydraulic drill was used to drill the well hole. The soil samples were collected continuously by alternating the downward movement of soil sampler and auger until an impermeable substratum was encountered. After extracting the soil from the split-spoon sampling device, the outermost layers of the soil core were cut away, so as to eliminate any contamination from the sampling device, and a portion of the residual soil sample preserved in a plastic container for later laboratory analysis. The remainder of the residual soil sample was then

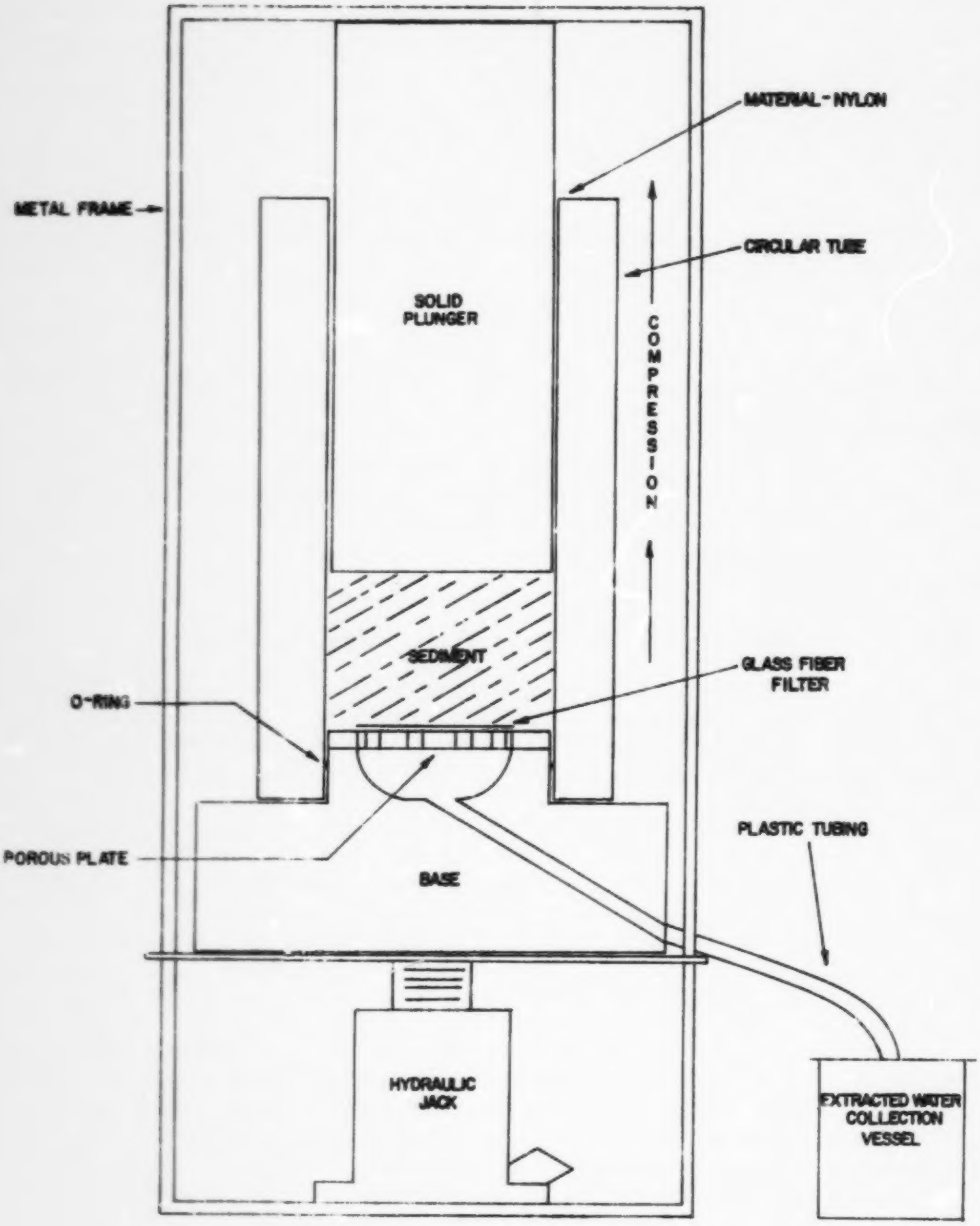
MATERIAL - NYLON
METAL FRAME
CIRCULAR TUBE
SOLID PLUNGER
COMPRESSION
SEDIMENT
GLASS FIBER FILTER
O-RING
PLASTIC TUBING
POROUS PLATE
BASE
HYDRAULIC JACK
EXTRACTED WATER COLLECTION VESSEL

FIGURE 5. CROSS-SECTION OF INTERSTITIAL WATER EXTRACTOR

hydraulically compressed with the nylon interstitial water extraction device illustrated in Figure 5. It was necessary to perform the extraction as soon as possible because any delay could alter the composition of the interstitial water, and no technique for preservation was available. A portion of the extracted interstitial water was then immediately analyzed for pH, conductivity, sulfate, alkalinity, and hardness. The remaining water was filtered through a 0.45 micron filter pad and acidified (HNO_3) for later laboratory analysis of metals.

The interstitial water extraction device was made of inert nylon. All parts were machined to fit with little or no water loss during operation. Actually, however, after many hours of use, extracted water began to leak out between the solid plunger and its sheath (the circular tube). This was a result of sand getting between the plunger and circular tube and the subsequent scoring of each during operation. A harder material, perhaps teflon, and more precise machine work would undoubtedly correct some of this problem. Operation of the extraction device was quite simple, but required a great deal of strength for optimum results. To operate the device, the solid plunger was removed from the circular tube and glass fiber filters (usually two) placed over the porous plate. A portion of subsoil sample collected within the zone of saturation was then placed inside the circular tube. The amount of subsoil compressed at one time varied depending on its composition. Clay material often required compression of several portions of a sample in order to obtain the needed volume of water, while a larger quantity of sand could be compressed with the same result. The amount of subsoil used per compression ranged from approximately 400 to 800 grams. After placing the subsoil in the circular tube, the solid plunger was inserted and the whole extraction device installed in the metal holding frame. A three-ton hydraulic jack was then used to force the base and plunger together, compressing the subsoil and forcing the water through the glass fiber filters to the collection vessel.

The volume of interstitial water obtained in this manner ranged from 6 to 30 milliliters per compression, or, by rough estimate, 4 to 15 percent of the subsoil's moisture content.

At all locations except J1 and J8, and at selected elevations (usually upon encountering a change in strata), undisturbed soil samples were collected for laboratory determinations of horizontal and vertical permeabilities, grain size classification, moisture content, and bulk density. (The results of these determinations are presented in Table 3, and the analytical methods in appendix A.) This was normally done by offsetting from the original sampling bore hole and drilling down to the predetermined sampling depth. The undisturbed samples were collected by hydraulically pushing a cylindrical tube (a Shelby tube) having a length of 76 cm and a diameter of 8.9 cm through the desired sampling area. The Shelby tube, with sample, was then extracted from the well hole and both ends sealed with paraffin wax to prevent moisture loss.

TABLE 3. PERMEABILITY, DENSITY, GRAIN-SIZE DISTRIBUTION,* AND MOISTURE CONTENT OF SUBSOILS COLLECTED FROM ASH DISPOSAL SITE - PLANT J

Sampling Location	Depth (m)	Vertical permeability (cm/s)	Horizontal permeability (cm/s)	Gravel (%)	Sand (%)	Silt (%)	Clay (%)	Density (g/cm^3)	Moisture (%)
J2	15.3	6.3×10^{-8}	7.4×10^{-8}	0	8	54	38	1.48	25.7
J3	14.1	1.3×10^{-6}	7.4×10^{-5}	3	25	63	9	1.42	24.6
J4	7.4	2.8×10^{-7}	6.6×10^{-8}	0	40	41	19	1.68	20.9
J4	9.7	3.1×10^{-6}	8.8×10^{-6}	0	80	14	6	1.60	22.6
J5	6.6	4.0×10^{-7}	2.8×10^{-7}	0	33	45	22	1.60	24.3
J6	7.4	4.4×10^{-7}	2.5×10^{-6}	0	29	51	20	1.48	26.7
J6	14.5	1.4×10^{-6}	1.3×10^{-6}	0	82	13	5	1.79	13.9
J7	12.9	6.1×10^{-6}	1.4×10^{-5}	0	69	24	7	1.45	20.7
J7	5.1	1.7×10^{-7}	2.6×10^{-7}	0	25	47	28	1.56	23.0

*Textural classification of soil fractions as per American Society for Testing and Materials designation, where: clay <0.005 mm, silt 0.005-0.074 mm, sand 0.074-4.75 mm, and gravel >4.75 mm.

After the original split-spoon sampling was completed, the void that had been produced by the action of the hollow-stem auger was cleaned out and a groundwater monitoring well installed. Each well was constructed of schedule 80 (0.64 cm wall thickness) polyvinyl chloride (PVC) pipe that had an outside diameter of 11.4 cm. The bottom 45 cm of each PVC well was perforated with 0.95 cm drill holes to allow groundwater inflow. Each PVC well was lowered to the bottom of the well hole and the annular space created between the perforated PVC pipe and the side of the well hole filled with pea gravel to some approximate height above the perforations, usually about 0.6 meters; this served to filter the inflow of solids into the well and prevent clogging. A layer of fine sand (approximately 0.3 meters thick) was placed in the annular space above the pea gravel filter. This functioned as a barrier between the pea gravel filter and a bentonite slurry placed in the annular space above the sand. The bentonite slurry extended from the top of the fine sand upwards to the surface of the water table and served to prevent water from channeling down the side of the PVC pipe. The remaining annular space above the bentonite slurry was filled with soil extracted from the original hole. At the point where the well casing entered the ground, a 0.5 meter diameter concrete apron, sloping away from the well, was constructed. This was done to further inhibit water from channeling down the side of the casing.

Fourteen wells were installed at the eight locations at plant J. Multiple wells were installed at locations J2, J3, J4, J5, J6, and J7 to enable the sampling of leachate from different substrata. Table 4 gives the depth of each well, the water table elevation at time of installation, and the type of stratum sampled.

Groundwater Sample Collection

To ensure that contamination of monitoring well samples did not occur from lowering a sampling device into the wells, groundwater samples were collected with a gas lift pump as illustrated in Figure 6. Cylinders of commercial argon or nitrogen gas containing less than 0.5 ppm oxygen were used during sample collection to minimize oxidation of the samples.

The gas cylinders were equipped with a pressure regulator and hose. With the hose attached to the Shrader valve at the well head, the regulator was adjusted to deliver 4218 to 7031 kgs/sq meter (6 to 10 psi). The gas flowed down the quarter-inch flexible tubing and into the bottom of the half-inch rigid plastic pipe, and lifted the water in the pipe to the surface where it was collected. To avoid collecting a water sample that may have set in a well for several weeks (and no longer would be representative of the surrounding ground water), at least one water volume of each well was pumped out prior to collecting a sample for analysis. After collection, water samples were preserved and shipped to the laboratory for analysis (see section 5).

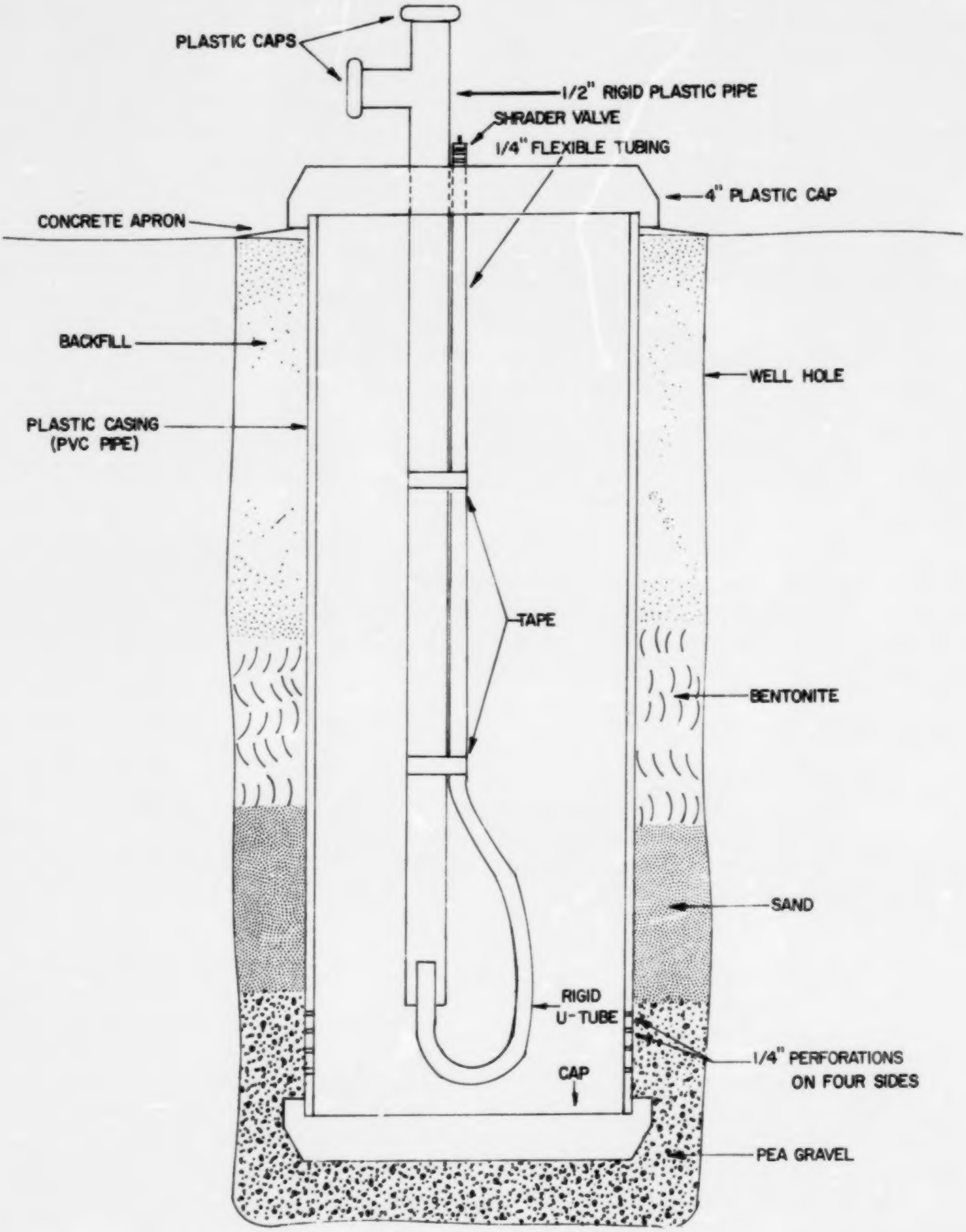
PLASTIC CAPS
1/2" RIGID PLASTIC PIPE
SHRADER VALVE
1/4" FLEXIBLE TUBING
4" PLASTIC CAP
CONCRETE APRON
BACKFILL
WELL HOLE
PLASTIC CASING (PVC PIPE)
TAPE
BENTONITE
SAND
RIGID U-TUBE
1/4" PERFORATIONS ON FOUR SIDES
CAP
PEA GRAVEL

FIGURE 6. CROSS-SECTION OF GROUNDWATER SAMPLING WELL

TABLE 4. GROUNDWATER SAMPLING WELL DEPTHS, WATER TABLE ELEVATIONS, AND SUBSOIL STRATUM SAMPLED AT PLANT J

Well	Well depth (meters)	Elevation at well bottom[a]	Water table elevation[a]	Type of stratum sampled[b]
J1	8.5	224.8	231.28	Shale
J2	14.0	219.4	230.19	Silty clay
J3	12.8	216.7	227.75	Silty sand
J3A	8.2	221.4	227.81	Coal ash
J4	7.6	221.6	225.11	Sand
J4A	3.6	225.6	c	Clayey silt
J5	8.5	220.7	225.64	Sand
J5A	3.6	225.7	c	Clayey silt
J5B	8.2	221.1	c	Sand
J6	4.1	224.4	224.15	Sand
J6A	11.8	216.8	c	Clayey silt
J7	14.0	213.4	226.10	Clay
J7A	4.2	223.0	226.10	Sand
J8	7.5	226.6	230.90	Shale

[a] Elevation above mean sea level (meters).
[b] Monitoring well casing perforated within these strata.
[c] Not measured.

TABLE 5. COMPARISON OF DISSOLVED OXYGEN CONCENTRATIONS IN GROUNDWATER SAMPLES COLLECTED BY PUMPING WITH NITROGEN AND AIR AT PLANT J

Well	*In situ*[a] dissolved oxygen	Dissolved oxygen in sample: Pumped with nitrogen	Dissolved oxygen in sample: Pumped with air
J2	0.5 mg/l	1.0 mg/l	20 mg/l
J3	0.2 mg/l	0.5 mg/l	8.3 mg/l
J3A	0.5 mg/l	0.2 mg/l	7.4 mg/l
J4	0.6 mg/l	0.2 mg/l	-
J4A	0.6 mg/l	0.7 mg/l	-

[a] *In situ* concentration after recovery from wasting one well water volume.

The validity of using a gas, such as nitrogen, to collect groundwater samples is supported by the data in Table 5. These data indicate that less change will occur in the dissolved oxygen concentration in the ground water by using nitrogen gas to pump the wells rather than by using air, and that the difference is quite significant.

Plant L - Groundwater Sampling

Groundwater monitoring wells were installed at 11 locations in and around the coal-ash disposal area at plant L (Figure 4). Two of the eleven locations, L10 and L11, are located hydraulically upgradient from the ash disposal area and function as background locations. Sites L6, L8, and L9 are in successively older sections of the ash disposal area and for the most part are no longer inundated. Locations L8 and L9 have some vegetative cover, while L6 is barren and partially inundated. Location L7 is hydraulically downgradient from the disposal area and L1, L2, L3, L4, and L5, are situated along the active disposal area's peripheral retainer dike.

Eighteen groundwater monitoring wells were installed at plant L. Multiple wells were installed at seven locations in order to sample different substrata. The depth of each well, the water table elevation, and the type of substratum from which water samples were collected are presented in Table 6.

Plant L's monitoring well design, and procedures for their installation, are essentially the same as described for plant J. However, at plant L, several of the monitoring wells were constructed using schedule 40 PVC pipe (0.32 cm wall thickness) with an outer diameter of 8.8 cm (3-1/2 inches). This smaller pipe proved to be easier to handle and install with no observed loss in sampling performance. Split-spoon soil sample collections, interstitial water extractions, undisturbed Shelby tube samples, and groundwater sample collection procedures at plant L are the same as described for plant J. The results of the permeability, density, grain, size distribution, and moisture content determinations on the undisturbed soil samples collected at plant L are presented in Table 7.

LABORATORY ATTENUATION STUDIES

During the project design phase, several possibilities were considered for generating, or simulating, an ash leachate in the laboratory suitable for use in an attenuation study. However, after the groundwater sampling wells were installed and leachate samples analyzed, it became apparent that the most representative water to use, and the most easily obtainable, was the actual coal-ash leachate collected *in situ*. The coal-ash leachate used in the laboratory attenuation studies was collected from groundwater sampling well L6A, at plant L. This well is approximately 10.6 meters deep and

TABLE 6. GROUNDWATER SAMPLING WELL DEPTHS, WATER TABLE ELEVATIONS, AND SUBSOIL STRATUM SAMPLES AT PLANT L

Well	Well depth (m)	Elevation at well bottom[a]	Water table elevation[a]	Type of stratum sampled
L1	10.67	179.72	183.22	Silt-clay
L1A	6.10	184.28	-	Silt-clay
L2	13.72	177.81	182.22	Silt-clay
L2A	6.10	185.76	186.50	Silt-clay
L3	13.41	178.13	181.51	Silt-clay
L3A	12.50	178.98	181.48	Silt-clay
L4	15.85	176.03	182.52	Silt-clay
L4A	6.10	185.44	182.60	Silt-clay
L5	15.24	175.89	183.03	Silt-clay
L5A	8.53	182.77	186.58	Silt-clay
L6	14.33	179.23	186.85	Silt-clay
L6A	10.67	182.54	186.81	Silt-clay
L7	8.84	175.04	182.10	Silt-clay
L8	11.89	179.51	187.55	Silt-clay
L9	8.53	183.13	189.08	Silt-clay
L9A	5.49	186.04	189.58	Silt-clay
L10	19.51	177.06	183.98	Silt-clay
L11	17.68	174.97	183.50	Silt-clay

[a] Elevation above mean sea level (m).

TABLE 7. PERMEABILITY, DENSITY, GRAIN-SIZE DISTRIBUTION,* AND MOISTURE CONTENT OF SUBSOILS COLLECTED FROM ASH DISPOSAL SITE - PLANT L

Sampling location	Depth (m)	Vertical permeability (cm/s)	Horizontal permeability (cm/s)	Sand (%)	Silt (%)	Clay (%)	Density (g/cm^3)	Moisture (%)
L2	13.8	1.4×10^{-8}	0.2×10^{-8}	23	48	29	1.72	19.2
L2A	5.8	6.3×10^{-8}	1.7×10^{-7}	30	18	31	1.66	18.7
L3	13.4	6.7×10^{-8}	5.8×10^{-8}	15	31	50	1.03	56.1
L3A	6.6	6.9×10^{-9}	1.1×10^{-8}	27	24	36	1.77	17.5
L3A	11.0	2.7×10^{-8}	1.2×10^{-8}	10	15	68	1.43	31.6
L4	13.4	3.7×10^{-8}	5.5×10^{-8}	14	21	43	1.28	36.5
L4	13.9	4.4×10^{-8}	3.4×10^{-8}	4	54	42	1.23	38.0
L4A	10.1	1.9×10^{-8}	2.0×10^{-8}	23	28	41	1.72	18.0
L5	8.3	1.4×10^{-8}	1.7×10^{-8}	15	34	51	1.64	23.2
L5	9.0	4.3×10^{-8}	7.4×10^{-9}	29	26	40	1.60	22.0
L6	10.7	6.6×10^{-6}	5.6×10^{-6}	54	42	4	1.45	24.3
L6	12.7	1.2×10^{-8}	5.7×10^{-9}	13	31	56	1.62	24.2
L7	8.8	55.2×10^{-8}	45.0×10^{-8}	10	65	25	1.06	57.5
L8	3.0	5.6×10^{-8}	2.3×10^{-8}	14	41	45	1.57	24.6
L8	0.8	3.0×10^{-4}	1.5×10^{-4}	37	58	1	1.18	35.2
L8	5.1	1.9×10^{-8}	7.4×10^{-9}	1	22	77	1.44	32.7
L9A	5.9	2.0×10^{-8}	1.9×10^{-8}	9	36	55	1.55	26.5
L10	16.6	2.3×10^{-8}	4.7×10^{-8}	5	15	80	1.34	37.3
L11	5.9	6.3×10^{-8}	2.8×10^{-8}	30	28	42	1.64	22.9

*Textural classification of soil fractions as per American Society for Testing and Materials designation, where: clay <0.005 mm, silt 0.005-0.074 mm, sand 0.074-4.75 mm, and gravel >4.75 mm.

terminates at the interface of the ash and the original soil. Only the bottom 45 cm of the well is perforated to allow leachate inflow. The water collected at this well has thus percolated downward through approximately 10 meters of ash. Leachate from plant L was selected because it could be transported to the laboratory the quickest.

After deciding that field collection was the optimum method for obtaining a leachate sample, there were collection problems that needed to be surmounted.

Preliminary in situ measurements indicated that anoxic conditions existed in the leachate environment, and if these conditions were not maintained during collection, transportation, and storage, alterations in the chemical characteristics of the leachate would result (simply allowing the leachate to come in contact with air would cause precipitates to form). This problem was alleviated by using argon gas to pump the leachate to the well head. At the well head, tygon tubing was connected to the 1.27 cm pipe that expelled the sample, and the other end to a 20-liter plastic receiving carboy, which was closed to the atmosphere. After wasting one well volume, the collection apparatus was purged with argon gas and then connected to the well head for sample collection. By sampling in this manner it was possible to maintain anoxic conditions in the leachate. After sample collection was completed, an argon atmosphere was maintained over the leachate in the carboy during transportation to the laboratory. Argon gas was used in place of nitrogen in the attenuation study because it contained less oxygen (<0.1 mg/l). In addition, argon is heavier than nitrogen and air and tended to form a blanket over the leachate to aid in the maintenance of anoxic conditions.

In the laboratory, the carboy was placed into a controlled temperature compartment maintained at 20°C under an atmosphere of argon. Once temperature equilibrium was established (approximately two days), attenuation studies were performed with the following materials: (1) soil taken from the ash pond dike at plant L, (2) soil taken from the ash pond dike at plant J, and (3) kaolinite. Each of these materials was homogenized and mixed with equal volumes of silica and rehomogenized prior to packing into columns. It was necessary to mix these materials with silica so that flow through the columns could be sustained. The fine clay material tended to swell and clog upon wetting, inhibiting or completely stopping the flow of leachate. The silica increased the permeability of the mixture and allowed the maintenance of flow through the column. The effect of the silica was not determined in this study, but it was assumed to be negligible because of the nonreactive nature of the silica particles, and the fact that each column had the same amount of silica, so the relative effects would be nearly the same.

Into each column (a 25-ml buret with an inside diameter of 1.2 cm), 11.64 grams of soil-silica mixture (1:1 volume ratio) was packed, at a density approximating the field conditions of 1.6 grams

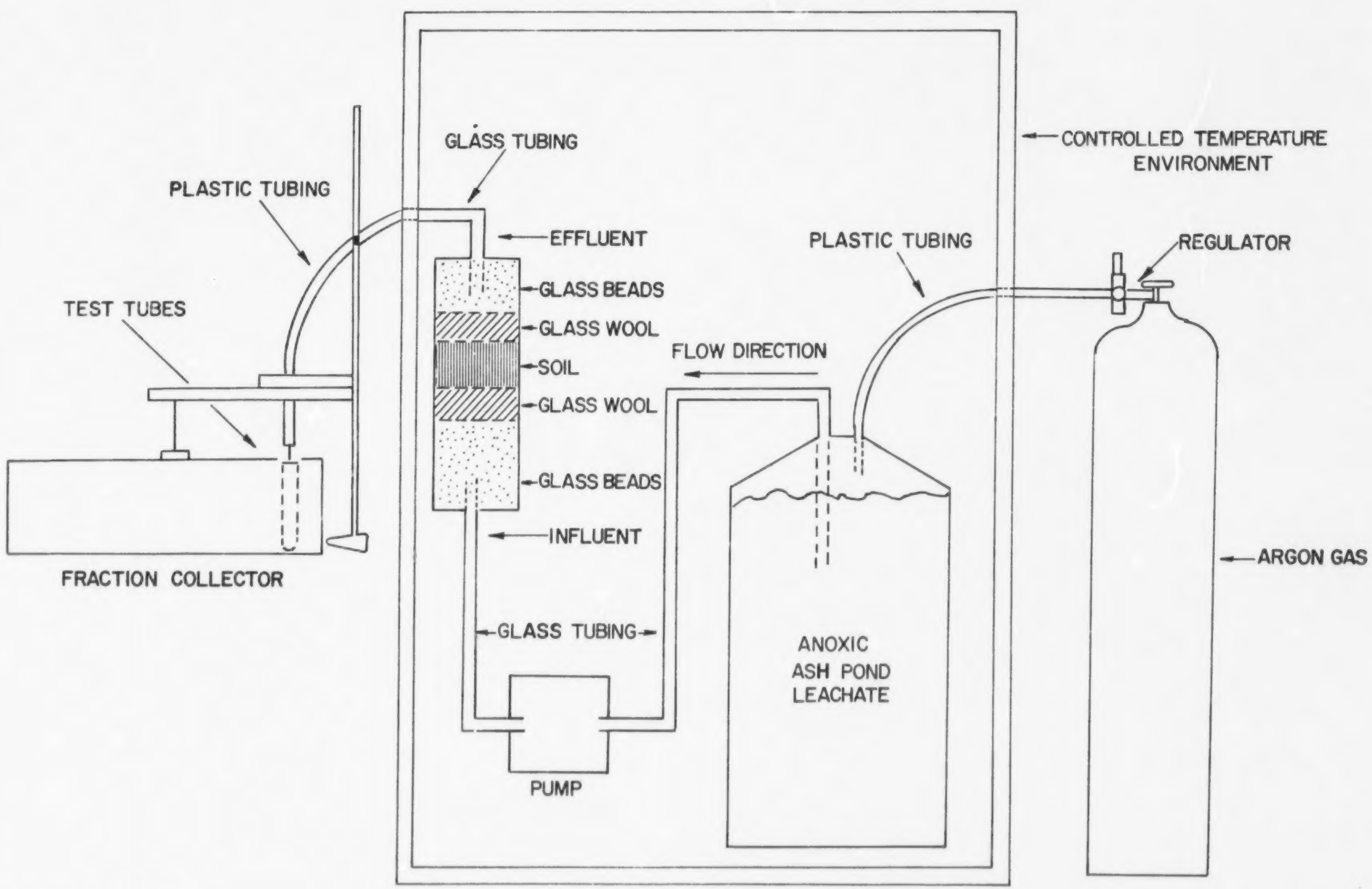
GLASS TUBING
PLASTIC TUBING
CONTROLLED TEMPERATURE ENVIRONMENT
EFFLUENT
PLASTIC TUBING
REGULATOR
GLASS BEADS
TEST TUBES
GLASS WOOL
SOIL
FLOW DIRECTION
GLASS WOOL
GLASS BEADS
INFLUENT
ARGON GAS
FRACTION COLLECTOR
GLASS TUBING
ANOXIC ASH POND LEACHATE
PUMP

FIGURE 7. COLUMN ELUTION APPARATUS

per cubic centimeter. Both ends of the soil-silica mixture were packed with glass wool and glass beads to maintain the integrity of the soil column. The column was set up in a controlled temperature chamber (see Figure 7) to maintain 20°C. The leachate was pumped from the plastic carboy with a low flow, teflon-coated pump, up through the soil column to allow air to escape and ensure saturation. The effluent from the column was then collected in glass test tubes predosed with 0.1 ml nitric acid. Effluent flow was adjusted as needed to approximately 0.1 ml per minute. Sample collection was accomplished by photoelectrical measurements of the column effluent volume, coupled with a rotating automatic fraction collector. Effluent samples were collected during the three attenuation studies until the calcium exchange capacity of each soil-silica mixture was theoretically exceeded (this was estimated from calculation). The effluent from each column was collected in 30 ml test tubes which were composited to make up 6 effluent samples per column. After compositing, the samples were analyzed for the constituents listed in Table 8. Procedures for these analyses are given in appendix A. In addition, each of the soils and clays were subjected to powder X-ray diffraction analysis for their relative amounts of montmorillite, kaolinite, illite, and quartz. Each was also analyzed for the constituents listed in Table 8 (see appendix A for description of soil procedure).

TABLE 8. CONSTITUENTS ANALYZED IN COLUMN ATTENUATION STUDIES

Calcium	Copper
Magnesium	Chromium
Sodium	Zinc
Potassium	Nickel
Iron	Cadmium
Manganese	Lead
Sulfate	Aluminum
Barium	Beryllium
Mercury	Selenium

SECTION 6

COAL ASH LEACHATE FIELD INVESTIGATIONS

In this section, the results of analyses performed on soil core, interstitial water, and groundwater samples collected at plants J and L are presented.

SOIL CORE ANALYSES

The split-spoon soil cores collected at plants J and L, as described in the section on Methodology, were analyzed in the laboratory for the chemical constituents listed in Table 9. The analytical procedures used in these analysis are described in appendix B.

TABLE 9. CHEMICAL ANALYSIS PERFORMED ON SPLIT-SPOON SOIL CORES

- Aluminum
- Arsenic
- Barium
- Beryllium
- Calcium
- Cadmium
- Chromium
- Copper
- Iron
- Magnesium
- Mercury
- Nickel
- Lead
- Selenium
- Sulfate
- Zinc

At nearly all sampling locations at plants J and L, soil-core samples were taken from ground surface to bedrock at various vertical intervals depending on the type of substratum encountered. The purpose for analyzing these vertical strata profiles for the constituents in Table 9 was to determine the extent of leachate migration downward and away from the ash disposal area by comparing the vertical and horizontal distribution of constituents in the substrata. In addition, the concentration differentials between various strata were used to compare their relative capacities for attenuating ash leachate.

The data presented in Tables 10 and 11 are a result of the chemical analyses performed on the soil cores collected at plants J and L, respectively.

TABLE 10. SOIL-CORE ANALYSIS AT PLANT J[a]

Sampling location	Depth (m)	Strata	Al	As	Ba	Be	Ca	Cd	Cr	Cu	Fe	Hg	Mg	Ni	Pb	Se	SO$_4$	Zn
J1	0.7	Clay-silt	160	11	130	-	1,200	<1	30	20	30,000	<0.1	-	25	18	<2	81	57
	1.3	Clay-silt	140	-	130	-	1,600	<1	26	31	21,000	<0.1	-	28	14	-	49	55
	1.9	Clay-silt	160	11	240	-	4,100	<1	29	30	26,000	<0.1	-	39	18	-	130	60
	2.5	Clay-silt	150	-	180	-	4,200	<1	31	28	22,000	<0.1	-	39	21	<2	28	64
	3.2	Clay-silt	64	-	140	-	3,300	<1	9	16	14,000	<0.1	-	25	81	-	40	38
	3.7	Clay-silt	160	-	140	-	3,900	<1	37	28	27,000	<0.1	-	45	19	-	46	96
	4.0	Clay-silt	120	<4	120	-	4,800	<1	32	29	21,000	<0.1	-	40	22	<2	71	46
J2	1.3	Ash	60	48	130	-	2,200	<1	10	24	8,300	<0.1	-	15	<5	2	2,500	21
	3.3	Ash	56	-	100	-	3,700	<1	31	25	6,300	<0.1	-	15	7	-	500	23
	5.7	Ash	83	-	140	-	2,400	<1	20	30	13,000	<0.1	-	13	7	-	240	20
	8.1	Ash	470	-	110	-	2,000	<1	12	21	13,000	<0.1	-	11	9	-	230	13
	13.5	Clay-silt	83	-	130	-	1,200	<1	7	16	9,000	<0.1	-	13	22	2	120	43
	14.0	Clay-silt	21,000	12	260	-	5,200	-	22	31	13,000	-	1,600	22	22	<1	67	27
	14.1	Clay-silt	620	-	130	-	1,000	<1	13	9	3,800	<0.1	-	<5	20	-	79	32
	14.6	Clay-silt	9,400	-	130	<1	970	<1	16	17	5,300	-	940	9	35	-	120	40
	15.0	Clay-silt	79	-	89	-	1,000	<1	17	16	30,000	<0.1	-	14	32	-	120	48
	15.5	Clay-silt	2,200	-	39	-	510	-	6	4	8,400	-	300	<5	14	-	320	12
	16.0	Sand	420	-	37	-	1,000	<1	11	11	10,000	<0.1	-	12	21	-	72	31
	16.4	Sand	3,900	-	74	<1	350	<1	10	8	4,700	-	590	6	38	-	110	83
	16.9	Sand	240	-	42	-	300	<1	7	11	25,000	<0.1	-	6	9	-	120	20
	17.3	Sand	1,000	-	-	-	460	-	9	<2	2,900	-	140	<5	7	<1	-	8
	17.8	Sand	360	-	47	-	400	<1	9	16	3,800	<0.1	-	5	<5	<2	130	140
J3	2.2	Ash	4,900	-	79	<1	1,200	<1	6	23	4,900	0.7	290	6	15	<2	3,600	5
	3.2	Ash	44,000	-	470	4	3,700	3[b]	47	72	30,000	0.52	3,000	56	69	-	590	90
	4.4	Ash	20,000	-	31	-	4,600	-[b]	23	37	14,000	<0.1	1,400	20	21	-	470	24
	10.2	Clay-silt	8,000	6	91	-	1,000	-[b]	11	14	13,000	<0.1	720	12	29	-	<4	39
	11.0	Sand	4,200	22	53	<0.1	550	<1	6	6	19,000	<0.1	340	<5	11	-	<4	12
	11.1	Sand	4,500	-	77	<1	520	<1	6	6	5,000	-	650	7	5	-	84	22
	11.5	Sand	-	-	-	-	-	-	-	-	-	<0.1	-	-	-	-	-	-
	12.1	Sand	2,300	-	30	-	770	-	<5	2	2,200	-	430	<5	7	-	<4	13
	13.4	Sand	2,700	-	45	-	800	-	<5	12	3,200	<0.1	650	<5	10	-	<4	19
	14.1	Sand	2,900	-	32	<1	300	<1	6	2	1,800	0.27	460	5	<5	<2	60	16
	14.5	Sand	-	-	-	-	290	-	-	-	-	-	360	-	-	-	-	-
	14.9	Sand	6,900	-	86	<1	870	1	13	8	8,900	0.28	2,400	16	8	<2	350	32
	15.0	Shale	16,000	-	180	2	16,000	2	35	16	20,000	0.20	8,600	39	13	<2	170	67

TABLE 10 (continued)[a]

Sampling location	Depth (m)	Strata	Al	As	Ba	Be	Ca	Cd	Cr	Cu	Fe	Hg	Mg	Ni	Pb	Se	SO_4	Zn
J4	1.7	Clay-silt	4,100	60	75	-	12,000	-	8	3	34,000	0.93	280	13	17	-	14,000	2
	3.5	Clay-silt	5,100	-	46	-	1,200	-	6	< 2	8,300	< 0.1	370	5	15	-	< 4	10
	5.0	Clay-silt	11,000	-	54	< 1	160	2	12	7	21,000	0.3	460	6	28	22	1,800	23
	6.5	Clay-silt	6,300	< 4	23	-	440	-	11	< 2	25,000	< 0.1	420	5	13	-	800	13
	8.0	Sand	3,900	-	54	< 1	160	< 1	< 5	< 1	3,700	-	300	< 5	7	-	130	12
	9.6	Sand	1,300	-	12	-	400	-	< 5	< 2	2,200	< 0.1	190	< 5	3	-	< 4	2
	11.1	Shale	11,000	-	140	3	970	2	30	18	41,000	0.28	2,900	53	54	< 2	180	86
J5	3.9	Clay-silt	12,000	-	32	1	330	1	10	8	14,000	0.23	600	8	26	< 2	340	30
	7.6	Clay-silt	7,000	-	36	< 1	160	< 1	7	6	14.000	-	350	7	21	-	5,600	17
	10.0	Clay-silt	3,800	-	16	-	420	-	9	< 2	13,000	< 0.1	230	< 5	11	-	< 4	9
	11.8	Sand	4,300	-	32	< 1	260	1	< 5	4	1,900	0.55	380	5	< 5	< 2	150	16
	12.2	Shale	20,000	-	180	1	1,800	1	35	29	16,000	-	6,800	46	8	-	400	94
	12.3	Shale	17,000	-	190	1	1,800	1	34	24	23,000	-	8,700	58	11	-	130	86
J6	1.9	Ash	8,900	-	160	< 1	1,400	2	16	32	38,000	1.2	410	18	25	< 2	3,300	9
	4.8	Clay-silt	11,000	-	28	< 1	480	1.0	13	10	18,000	-	520	8	19	-	100	26
	8.2	Clay-silt	5,900	-	80	-	600	-	14	< 2	11,000	< 0.1	800	10	12	-	< 4	24
	9.6	Clay-silt	-	-	-	-	460		-	-	-	-	800	-	-	-	-	-
	11.5	Clay-silt	3,800	-	45	1	390	2	10	8	9,500	0.17	540	5	< 5	< 2	34	21
	12.8	Clay-silt	6,300	-	78	-	910	-	20	< 2	12,000	< 0.1	930	10	14	-	< 4	26
	14.1	Sand	1,700	-	46	< 1	1,500	< 1	< 5	2	1,800	0.48	390	5	< 5	< 2	170	15

[a] Values in μg/g.

[b] Not analyzed.

TABLE 11. SOIL-CORE ANALYSES AT PLANT L[a]

Sampling location	Depth (m)	Strata	Al	As	Ba	Be	Ca	Cd	Cr	Cu	Fe	Hg	Mg	Ni	Pb	Se	SO_4	Zn
J7	0.7	Clay-silt	14,000	-	220	1	4,100	< 1	31	22	21,000	0.37	6,400	42	15	< 2	140	59
	1.6	Clay-silt	14,000	-	300	1	15,000	< 1	31	22	19,000	0.37	6,600	42	15	< 2	240	59
	2.5	Clay-silt	16,000	-	280	-	22,000	-	51	21	29,000	< 0.1	6,700	43	24	-	490	71
	3.5	Clay-silt	12,000	-	190	-	14,000	-	33	17	26,000	< 0.1	5,000	44	20	-	290	48
	4.5	Clay-silt	12,000	-	57	< 1	1,000	< 1	12	9	17,000	-	1,100	5	30	-	350	25
	5.0	Clay-silt	14,000	-	58	-	1,500	-	12	8	25,000	< 0.1	110	12	17	-	470	35
	6.8	Shad	5,100	-	31	< 1	150	< 1	10	2	18,000	-	500	< 5	24	-	120	19
	7.9	Sand	6,200	-	25	-	470	-	26	10	8,900	< 0.1	120	9	16	-	< 4	29
	8.8	Sand	5,900	-	29	-	550	-	11	6	8,400	< 0.1	960	10	13	-	< 4	18
	10.0	Sand	2,200	-	< 10	< 1	120	< 1	< 5	< 1	22,000	0.23	250	< 5	19	< 2	37	18
	11.2	Sand	2,700	-	15	-	240	-	8	6	2,300	< 0.1	370	< 5	6	-	76	9
	11.8	Sand	1,300	-	< 10	< 1	160	< 1	< 5	2	1,800	0.15	250	< 5	17	< 2	93	8
	13.4	Shale	1,500	-	430	2	2,300	1	39	4	21,000	1.1	6,100	57	29	< 2	7,000	77
J8	3.3	Shale	17,000	-	100	2	21,000	2	35	68	18,000	0.27	5,200	70	33	< 2	7,000	70
	4.0	Shale	18,000	-	110	1	4,100	2	43	12	21,000	-	7,000	41	24	-	3,600	67
	4.8	Shale	15,000	-	200	-	4,600	-	42	4	27,000	< 0.1	7,300	45	17	-	200	77
	6.3	Shale	18,000	-	310	1	11,000	1	46	42	22,000	-	8,500	43	28	-	160	76
	7.8	Shale	12,000	-	200	-	7,100	-	32	14	22,000	< 0.1	6,000	34	10	1	180	51
	9.2	Shale	18,000	-	180	1	4,200	1	44	27	24,000	0.28	8,600	51	22	< 2	93	74

TABLE 11. SOIL-CORE ANALYSES AT PLANT L[a]

Sampling location	Depth (m)	Strata	Al	As	Ba	Be	Ca	Cd	Cr	Cu	Fe	Hg	Mg	Ni	Pb	Se	SO_4	Zn
L1	2.4	Silty clay	13,000	<1	100	<1	82,000	<1	26	19	31,000	<0.1	1,800	13	28	<1	60	20
	4.3	Silty clay	17,000	<1	80	1	2,400	<1	23	17	28,000	0.2	820	7	15	<1	8	20
	6.7	Silty clay	15,000	<1	80	<1	1,200	<1	26	15	19,000	0.1	620	8	20	<1	50	25
	7.3	Silty clay	16,000	<1	70	2	2,000	<1	26	9	30,000	-	950	6	20	-	60	22
	9.1	Silty clay	16,000	3	110	1	89,000	<1	26	16	30,000	0.1	4,000	26	24	<1	60	48
	10.4	Silty clay	18,000	<1	80	1	5,400	<1	29	24	29,000	-	4,600	25	15	-	10	70
	11.6	Silty clay	10,000	<1	80	<1	93,000	<1	22	20	17,000	-	5,300	28	16	-	410	52
L2	2.1	Silty clay	10,000	<1	80	<1	2,200	<1	36	13	29,000	0.2	970	12	21	<1	100	38
	6.7	Silty clay	17,000	<1	100	2	1,200	<1	48	18	29,000	0.2	900	10	21	<1	46	42
	10.4	Silty clay	20,000	1	20	<1	730	<1	33	13	29,000	0.1	440	8	14	<1	8	19
	11.0	Silty clay	15,000	<1	120	2	2,400	<1	28	10	16,000	-	2,000	16	20	-	80	42
	12.8	Silty clay	12,000	<1	80	1	2,000	<1	20	6	12,000	0.2	1,400	9	18	<1	60	29
	13.5	Silty clay	11,000	<1	50	<1	2,400	<1	18	4	6,200	-	990	8	14	-	30	39
	13.6	Silty clay	3,800	<1	190	<1	160,000	<1	16	18	39,000	-	3,200	32	25	-	20	28
L3	3.7	Silty clay	15,000	<1	170	1	7,900	<1	45	10	52,000	<0.1	2,300	28	24	<1	26	70
	6.7	Silty clay	10,000	<1	40	1	380	<1	25	6	11,000	0.2	710	8	10	<1	60	26
	9.5	Silty clay	14,000	<1	40	<1	350	<1	34	8	23,000	<0.1	760	8	24	<1	60	27
	10.1	Silty clay	19,000	<1	120	<1	2,400	<1	32	10	19,000	-	3,300	13	23	-	160	24
	11.9	Silty clay	19,000	5	100	3	2,600	<1	36	22	97,000	-	3,900	48	31	-	60	78
	13.7	Silty clay	14,000	<1	80	1	240,000	<1	27	13	8,600	-	15,000	34	22	-	34	42
	14.9	Silty clay	26,000	<1	110	3	4,600	<1	48	32	49,000	0.1	12,000	57	41	<1	28	90
L4	3.7	Silty clay	16,000	7	80	1	1,800	<1	38	6	22,000	0.2	2,000	10	14	<1	1,000	30
	6.7	Silty clay	13,000	<1	60	<1	610	<1	39	7	23,000	<0.1	1,600	10	14	<1	60	36
	9.7	Silty clay	11,000	<1	100	<1	2,300	<1	26	8	30,000	0.2	1,500	12	15	<1	30	35
	9.8	Silty clay	10,000	<1	60	1	800	<1	12	10	11,000	-	1,000	7	12	-	300	39
	10.8	Silty clay	11,000	<1	40	<1	650	<1	15	4	6,100	0.1	400	<5	7	<1	20	18
	12.8	Silty clay	11,000	<1	80	1	1,200	<1	22	20	18,000	-	1,400	32	31	-	8	97
	14.6	Silty clay	13,000	<1	60	2	12,000	<1	27	9	14,000	-	8,400	18	14	-	20	40
	15.9	Silty clay	17,000	<1	40	1	1,600	<1	26	8	29,000	<0.1	1,600	11	18	<1	8	25

TABLE 11 (continued)

Sampling location	Depth (m)	Strata	Al	As	Ba	Be	Ca	Cd	Cr	Cu	Fe	Hg	Mg	Ni	Pb	Se	SO_4	Zn
L5	2.1	Silty clay	12,000	9	140	2	3,800	<1	34	8	26,000	0.2	2,000	11	18	<1	180	34
	5.2	Silty clay	11,000	<1	80	<1	900	<1	33	9	25,000	<0.1	1,700	10	16	<1	10	42
	6.7	Silty clay	17,000	1	60	<1	620	<1	34	8	30,000	0.2	1,300	10	21	<1	60	26
	8.2	Silty clay	18,000	<1	40	<1	420	<1	30	7	25,000	-	1,600	7	17	-	26	24
	10.1	Silty clay	10,000	<1	50	1	350	<1	31	14	30,000	-	1,500	10	18	-	10	25
	11.9	Silty clay	10,000	<1	20	<1	570	<1	28	18	30,000	0.2	1,600	10	16	<1	12	26
	15.2	Silty clay	12,000	1.0	60	<1	32,000	<1	29	13	34,000	-	3,200	13	19	-	19	58
L6	0.9	Ash	11,000	5	140	2	14,000	<1	32	27	13,000	<0.1	1,300	42	25	2	3,700	91
	1.5	Ash	15,000	3	110	2	13,000	<1	24	34	11,000	<0.1	1,000	41	31	2	5,900	120
	2.1	Ash	14,000	<1	200	1	7,300	<1	26	34	65,000	0.2	1,100	31	11	<1	60	73
	3.7	Ash	10,000	2	220	1	5,500	<1	26	18	65,000	0.2	660	34	16	<1	200	57
	5.2	Ash	14,000	1	140	<1	3,800	<1	19	18	35,000	0.2	740	24	10	<1	360	34
	6.7	Ash	15,000	4	240	2	13,000	2	45	20	51,000	0.2	1,300	29	23	1	940	130
	8.2	Ash	12,000	5	140	2	8,700	<1	21	13	53,000	<0.1	680	24	8	<1	190	77
	8.8	Ash	15,000	4	220	1	10,000	2	42	35	48,000	<0.1	1,200	29	24	<1	190	140
	10.1	Silty clay	15,000	<1	140	2	4,800	<1	28	20	50,000	<0.01	640	28	8	<1	200	52
	10.7	Silty clay	22,000	<1	90	1	1,400	<1	36	9	40,000	0.1	980	11	17	<1	34	47
	11.3	Silty clay	18,000	<1	80	<1	610	<1	29	9	32,000	-	790	8	18	-	60	24
	11.9	Silty clay	14,000	<1	120	<1	1,800	<1	34	4	28,000	0.1	920	14	16	<1	8	19
	12.5	Silty clay	19,000	1	260	1	3,200	<1	42	14	39,000	-	160	13	32	-	64	33
	13.1	Silty clay	20,000	<1	80	2	3,800	<1	34	8	49,000	0.2	1,900	11	28	<1	60	32
	13.7	Silty clay	25,000	<1	100	2	3,800	<1	37	14	41,000	-	2,800	18	21	-	26	55
	14.2	Silty clay	17,000	<1	170	1	6,500	<1	40	13	44,000	0.1	2,700	20	31	<1	60	64
L7	0.9	Silty clay	17,000	<1	90	2	5,900	<1	31	15	27,000	<0.1	2,800	11	18	<1	80	56
	2.4	Silty clay	22,000	<1	190	2	5,000	<1	29	35	31,000	-	3,100	21	23	-	60	130
	3.7	Silty clay	22,000	<1	230	2	2,300	<1	32	13	44,000	0.1	3,000	23	23	<1	120	83
	5.2	Silty clay	18,000	<1	160	2	2,500	<1	32	20	34,000	-	2,800	18	25	-	26	74
	6.7	Silty clay	10,000	<1	90	1	1,200	<1	17	9	16,000	-	1,300	8	9	-	60	36
	8.2	Silty clay	18,000	<3	160	2	8,000	<1	28	14	36,000	0.1	6,500	37	37	<1	28	85

TABLE 11 (continued)

Sampling location	Depth (m)	Strata	Al	As	Ba	Be	Ca	Cd	Cr	Cu	Fe	Hg	Mg	Ni	Pb	Se	SO_4	Zn
L8	0.9	Ash	12,000	<1	180	2	6,500	<1	37	21	60,000	<0.1	1,400	28	11	<1	700	47
	1.5	Ash	15,000	<1	320	2	7,600	<1	29	24	34,000	0.3	1,200	21	16	<1	3,400	45
	2.1	Ash	5,500	<1	180	<1	2,200	<1	21	12	46,000	0.1	640	16	13	<1	280	17
	2.7	Silty clay	13,000	<1	40	<1	830	<1	36	12	42,000	0.1	600	10	47	<1	360	49
	3.4	Silty clay	16,000	<1	40	1	740	<1	42	12	40,000	-	700	7	26	-	1,200	38
	5.2	Silty clay	15,000	14	40	1	1,000	<1	61	20	32,000	0.2	710	7	26	<1	100	79
	7.6	Silty clay	13,000	<1	160	2	53,000	<1	27	17	34,000	-	3,600	28	22	-	60	54
	10.1	Silty clay	12,000	<1	90	2	3,600	<1	29	25	33,000	-	1,600	16	27	-	100	67
	11.9	Silty clay	10,000	3	140	2	5,500	<1	19	5	63,000	0.1	2,800	18	14	<1	120	57
L9	0.9	Ash	10,000	<1	140	1	4,800	2	38	24	37,000	0.2	760	24	10	<1	50	93
	1.8	Ash	12,000	<1	200	2	5,200	<1	33	27	38,000	0.2	960	19	12	<1	36	42
	2.7	Silty clay	13,000	<1	300	2	8,500	<1	42	13	63,000	0.2	1,800	20	15	<1	60	31
	3.7	Silty clay	5,600	1	260	2	4,900	<1	21	28	21,000	0.2	860	10	14	<1	160	25
	4.6	Silty clay	7,000	20	270	3	5,800	<1	27	19	46,000	0.4	880	21	14	<1	240	39
	5.5	Silty clay	6,300	<1	90	1	1,300	<1	17	17	13,000	0.1	840	6	20	<1	180	49
	6.1	Silty clay	11,000	<1	50	2	430	<1	34	8	22,000	-	690	<5	15	-	60	18
	7.9	Silty clay	15,000	<1	120	3	4,200	<1	33	33	55,000	0.4	1,600	27	44	<1	80	48
	10.5	Silty clay	15,000	<1	160	3	8,000	<1	41	31	40,000	-	3,300	32	21	-	60	77
L10	2.1	Silty clay	11,000	11	40	<1	200	<1	45	12	37,000	0.1	330	7	15	<1	12	29
	5.2	Silty clay	4,500	<1	30	<1	170	<1	26	6	20,000	-	120	<5	14	-	60	13
	8.2	Silty clay	4,100	<1	20	<1	270	<1	17	9	13,000	-	160	<5	17	-	8	18
	12.8	Silty clay	11,000	24	20	1	330	<1	37	24	32,000	0.2	340	13	16	<1	60	66
	17.4	Silty clay	10,000	16	10	2	320	<1	39	26	41,000	0.2	400	23	22	<1	8	91
	20.4	Silty clay	13,000	<1	20	<1	360	<1	37	28	34,000	-	530	18	26	-	8	45
L11	3.7	Silty clay	9,900	<1	40	<1	380	<1	51	21	50,000	0.2	290	12	8	<1	8	24
	6.7	Silty clay	10,000	<1	40	<1	360	<1	37	16	40,000	-	760	9	23	-	60	22
	9.8	Silty clay	13,000	<1	40	1	650	<1	46	22	36,000	0.4	1,400	13	17	<1	60	48
	12.8	Silty clay	3,100	1	10	<1	490	<1	33	7	19,000	-	210	<5	14	-	8	16
	17.4	Silty clay	3,900	<1	80	1	830	<1	33	20	32,000	0.2	940	37	19	<1	10	41

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[a] Values in μg/g.

The most notable characteristic about the data from plant J (Table 10) is that the concentrations of most constituents are highly variable, both within and between sampling locations. The concentration of mercury, with two exceptions, was found to be below 1.0 μg/g. At sampling locations J1 and J8, the least variability (in terms of absolute differences) in concentrations was observed for most constituents. This is not surprising since both these locations were hydraulically upgradient from the ash disposal area and have homogeneous stratum types throughout their vertical profiles, albeit different from one another. The variable nature of the data is further illustrated in Table 12. This table gives the ranges of concentrations in each soil type measured at locations J2 through J7 combined, and also the ranges within each location. These data indicate that the more variable values are associated with the clay-silt, ash, and shale materials, while the sand contained a narrower range of concentrations. Locations J1 and J8 were omitted from the soil type comparisons because of their previously mentioned homogeneity. However, in the bottom portion of Table 12, where ranges of values are given for each sampling location, the lower variability at locations J1 and J8 relative to other locations is again indicated. At sampling locations J2 through J7, the magnitude of the variability is dependent on the constituent under consideration. For example, location J2 has the widest range of aluminum values, location J4 has the widest range of calcium values, and location J7 has the widest range of chromium concentrations.

The data from plant L (Table 11), although not nearly as variable as plant J's, exhibits some variability, both within and between, sampling locations. Beryllium, cadmium, and selenium values, like plant J's data, are less than or near their analytical detection limits, while concentrations of mercury were all measured below 0.5 μg/g. However, unlike the data from plant J, the two hydraulically upgradient sampling locations at plant L (L10 and L11) are no less variable than sampling locations downgradient from the ash disposal area. It should be noted that the strata types present at plant L consisted mostly of a homogeneous silty-clay material throughout the vertical profile. The variation in plant L's soil core concentrations is also illustrated in Table 13, where the range of concentration in each stratum measured and the ranges within each location are given.

The data in this table indicate that, except for selenium, sulfate, and zinc, the highest constituent concentrations are associated with the silty-clay material. At the bottom of Table 13, the range in concentration within each sampling location indicates that, unlike the control locations at plant J, plant L's upgradient control locations (L10 and L11) are nearly as variable as the sampling locations downgradient from the ash disposal area. Several parameters (iron, copper, chromium, zinc, lead, and nickel) actually demonstrate higher maximum concentrations in the control locations than several of the hydraulically downgradient locations.

TABLE 12. RANGES OF CONCENTRATIONS WITH EACH SOIL TYPE AND AT EACH SAMPLING LOCATION FOR THE SOIL CORE SAMPLES ANALYZED FROM PLANT J[a]

Soil type	Al	As	Ba	Be	Ca	Cd	Cr	Cu	Fe	Hg	Mg	Ni	Pb	Se	SO_4	Zn
Clay-silt	64-21,000	<4-60	16-300	<1-1.0	160-12,000	<1-2.0	6-37	<2-31	8300-34,000	<0.1-0.93	110-6700	<5-45	<5-81	<1-22	4-1400	2-96
Sand	240-6900	22	<10-86	<1-<0.1	120-1500	<1-1.0	<5-26	<1-16	1800-25,000	<0.1-0.55	120-2400	<5-16	<5-38	<2	<4-350	2-140
Shale	1500-20,000	-	100-430	1.0-3.0	970-21,000	1.0-2.0	30-46	4-68	16,000-41,000	<0.1-1.1	2900-8700	39-70	8-33	1.0-<2	93-7000	51-94
Ash	56-44,000	48	31-470	<1-4.0	1200-4600	<1-3.0	6-47	21-72	4900-38,000	<0.1-1.2	290-3000	6-56	<5-69	<2-2.0	230-3600	5-90
Sampling locations																
J1	64-160	<4-11	120-240	-	1200-4800	<1	9-37	16-31	14,000-30,000	<0.1	-	25-45	14-81	<2	28-130	38-96
J2	56-21,000	12-48	37-260	<1	300-5200	<1	6-31	<2-31	2900-30,000	<0.1	140-1600	<5-22	<5-38	<1-<2	67-2500	8-140
J3	2300-44,000	6-22	30-470	<0.1-4.0	290-16,000	<1-3.0	<5-47	2-72	1800-30,000	<0.1-0.7	290-8600	<5-56	<5-69	<2	<4-3600	5-90
J4	1300-11,000	<4-60	12-140	<1-3.0	160-12,000	<1-2.0	<5-30	<1-18	2200-41,000	<0.1-0.93	190-2900	<5-53	3-54	<2-22	<4-14,000	2-86
J5	3800-20,000	-	16-190	<1-1.0	160-1800	<1-1.0	<5-35	<2-29	1900-23,000	<0.1-0.55	230-8700	<5-58	<5-26	<2	<4-5600	9-94
J6	1700-11,000	-	28-160	<1-1.0	390-1500	<1-2.0	<5-20	<2-32	1800-38,000	<0.1-1.2	390-930	5-18	<5-25	<2	<4-3300	9-26
J7	1300-16,000	-	<10-430	<1-2.0	120-22,000	<1-1.0	<5-51	<1-22	1800-29,000	<0.1-1.1	110-6700	<5-57	6-30	<2	<4-7000	8-77
J8	12,000-18,000	-	100-310	1-2	4100-21,000	1.0-2.0	32-46	4-68	18,000-27,000	<0.1-0.28	5200-8600	34-70	10-33	1-<2	93-7000	51-77

[a] Values in μg/g.

TABLE 13. RANGES OF CONCENTRATIONS WITHIN EACH STRATA AT EACH SAMPLING LOCATION FOR THE SOIL CORE SAMPLES ANALYZED FROM PLANT L[a]

Strata	Al	As	Ba	Be	Ca	Cd	Cr	Cu	Fe	Hg	Mg	Ni	Pb	Se	SO_4	Zn
Ash	5,500-15,000	< 1-5	110-240	< 1-2	2200-14,000	< 1-2	19-45	13-35	11,000-65,000	< 0.1-0.3	640-1400	16-42	8-31	< 1-2	36-5500	17-140
Silty clay	3,100-26,000	< 1-24	10-300	< 1-3	320-240,000	< 1	12-51	4-35	6,100-97,000	< 0.1-0.4	120-15,000	< 5-57	7-47	< 1	8-3400	13-130
Sampling location																
L1	13,000-18,000	< 1-3	70-110	< 1-2	1200-93,000	< 1	22-29	9-24	17,000-31,000	< 1-0.2	620-5300	6-28	15-28	< 1	8-410	20-70
L2	3,800-20,000	< 1-1	20-190	< 1-2	730-160,000	< 1	18-48	4-18	6,200-39,000	0.1-0.2	440-3200	8-32	14-25	< 1	8-100	19-42
L3	10,000-26,000	< 1-5	40-170	< 1-3	350-240,000	< 1	25-48	6-22	8,600-97,000	< 1-0.2	710-15,000	8-57	10-41	< 1	26-260	26-90
L4	10,000-17,000	< 1-7	40-100	< 1-2	610-12,000	< 1	12-39	4-20	6,100-30,000	< 1-0.2	400-8400	< 5-32	7-31	< 1	8-1000	18-97
L5	10,000-18,000	< 1-9	20-140	< 1-2	350-32,000	< 1	28-34	7-18	25,000-34,000	< 1-0.2	1300-3200	7-13	16-21	< 1	10-180	24-58
L6	10,000-25,000	< 1-5	80-260	< 1-2	610-14,000	< 1-2	19-45	4-35	11,000-65,000	< 0.1-0.2	160-2800	8-42	8-32	< 1-2	8-5500	19-140
L7	10,000-22,000	< 1-< 3	90-230	< 1-2	1200-8000	< 1	17-32	9-35	16,000-44,000	< 1	1300-6500	8-37	9-37	< 1	26-120	36-130
L8	5,500-16,000	< 1-14	40-320	< 1-2	740-53,000	< 1	19-42	5-25	33,000-63,000	< 0.01-0.3	600-3600	7-28	11-47	< 1	60-3400	17-79
L9	5,600-15,000	< 1-20	50-300	1-3	430-8500	< 1-2	17-42	8-33	13,000-63,000	0.2-0.4	690-3300	< 5-32	10-44	< 1	36-240	18-93
L10	4,100-13,000	< 1-24	10-40	< 1-2	170-360	< 1	17-45	6-28	13,000-41,000	0.1-0.2	120-530	< 5-23	14-26	< 1	8-60	13-91
L11	3,100-13,000	< 1-1	10-80	< 1-1	360-830	< 1	33-51	7-22	19,000-50,000	0.2-0.4	210-1400	< 5-37	8-23	< 1	8-60	16-48

[a] Values in μg/g.

TABLE 14. CONCENTRATIONS IN ASH SAMPLES COLLECTED FROM ASH DISPOSAL AREAS - PLANTS J AND L[a]

Constituent	Plant J Mean	Plant J Range	Plant L Mean	Plant L Range
Aluminum	9,938.4	56-44,000	12,346.2	5,500-15,000
Arsenic	48	48	2.3	<1.0-5
Barium	151.4	79-470	186.9	110-320
Beryllium	2.5	<1.0-4	1.5	<1.0-2
Calcium	2,828.6	1,200-4,600	7,815.4	2,200-14,000
Cadmium	1.3	<1.0-3	1.2	<1.0-2
Chromium	21.3	6-47	30.2	19-45
Copper	33.1	21-72	23.6	12-35
Iron	12,785.7	4,900-30,000	42,769.2	11,000-65,000
Magnesium	1,563.3	290-3,000	995.4	640-1,800
Mercury	0.3	<0.1-0.7	0.2	<0.1-0.3
Nickel	19.4	6-56	27.8	16-42
Lead	19.0	<5-69	16.2	8-31
Selenium	2.0	<2-2	1.2	<1.0-2
Sulfate	1,161.4	230-3,600	1,200.5	36-5,500
Zinc	28.0	5-90	74.3	17-140

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[a] Values in mg/L.

The mean concentrations and range of values for the constituents listed in Table 9 were calculated for all ash samples collected at plants J and L. At plant J, ash samples were collected over various vertical intervals at sampling locations J2 and J3, and at plant L sampling locations L6, L8, and L9. The results of these calculations indicate (Table 14) that the mean concentrations of aluminum, barium, calcium, chromium, iron, nickel, sulfate, and zinc are highest in ash from plant L. Plant J, however, had the higher mean concentrations of arsenic, beryllium, cadmium, copper, mercury, lead, selenium, and magnesium. There are a multitude of reasons why the above elements would be partitioned as they are between the two plants; different coal sources, methods of firing the coal, and ash collection systems are the major reasons related to plant operations. The sample collection is undoubtedly another factor to consider. The age of the ash sample and its particle size characteristics may also affect concentrations within the sample. The longer coal ash has been exposed to the leaching process the more opportunity for the dissolution of ions, and at least one investigator[15] has shown that smaller ash particles contain higher concentrations of certain elements.

The variable nature of the constituents measured in the soil cores from plants J and L, precluded the use of this data for determining the extent of leachate migration. The natural variation of soils resulting from spatial differences in mineralology, organic content, and soil particle sizes makes the effects of leachate on constituent concentrations in the soil difficult or impossible to define. Determining differences in the attenuation capacity of the various substrata also suffers because the highly variable soil makes results ambiguous. In order to utilize soil core data to determine the magnitude of leachate migration, some means of eliminating or minimizing the natural variation will be needed. One approach may be to analyze only a certain particle size fraction of a sample for a contaminant. Another might be to separate the various components of a soil sample, such as organic and inorganic, and analyze separately. There are many approaches which might be considered, but the measurement of constituents in total soil samples, as this investigation indicates, does not appear to be a viable one.

INTERSTITIAL WATER ANALYSIS

During the collection of soil core samples from plants J and L, certain cores were selected for extraction and analysis of their interstitial water (the extraction methodology is given in section 4). The basis for selecting which cores were to be extracted was the apparent moisture content of the core and the density of the material under consideration. Both of these factors were evaluated in the field, based on field soil testing techniques, previous experience, and intuition. In all, 23 soil-core extractions were analyzed from plant J, and seven at plant L. The fewer number of samples extracted

TABLE 15. ANALYSIS OF EXTRACTED INTERSTITIAL WATER FROM PLANT J

	Well locations											
	J3	J3	J4	J4	J4	J4	J4	J5	J5	J5	J6	J6
Depth, m	13.4	14.1	5.0	6.5	8.0	9.6	11.1	6.7	8.4	11.8	5.0	6.5
Strata	Sand	Sand	Clay-silt	Clay-silt	Clay-silt	Clay-silt	Sand	Clay-silt	Sand	Sand	Clay-silt	Clay-silt
Aluminum, mg/L	3.2	3.15	180	190	60	< 0.2	5.2	15	62	8.0	-	5.5
Barium, mg/L	< 0.1	-	< 0.1	< 0.1	< 0.1	< 0.1	1.3	-	-	-	-	-
Beryllium, mg/L	-	-	-	-	< 0.01	-	-	-	-	-	-	-
Calcium, mg/L	56	15.5	470	680	350	130	170	270	310	87	-	31
Cadmium, mg/L	-	< 0.001	-	-	-	-	-	0.002	0.005	0.003	-	-
Chromium, mg/L	< 0.01	0.008	0.04	0.05	0.06	< 0.01	< 0.01	0.02	0.7	0.02	< 0.001	0.011
Copper, mg/L	0.3	0.02	0.2	0.3	0.3	< 0.1	< 0.1	0.20	0.27	0.63	0.2	0.08
Iron, mg/L	15	0.82	3300	2400	1200	1.0	120	1000	1000	10	38	10
Magnesium, mg/L	14	-	200	220	91	33	31	-	-	-	-	-
Mercury, mg/L	-	< 0.01	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.01	< 0.01	< 0.02	-
Nickel, mg/L	< 0.5	< 0.05	0.9	< 0.5	0.8	< 0.5	< 0.5	0.35	0.5	0.2	< 0.5	< 0.5
Lead, mg/L	-	< 0.006	0.76	0.58	0.42	0.09	0.11	0.019	0.017	0.12	< 0.05	0.066
Selenium, mg/L	-	< 0.05	-	-	-	-	-	< 0.10	< 0.05	< 0.05	-	-
Sulfate, mg/L	-	-	6800	4800	2300	380	680	-	-	-	100	-
Zinc, mg/L	0.7	0.02	4.3	3.5	4.8	5.8	0.6	1.3	2.6	2.1	5.1	1.4
pH, std. units	7.3	8.0	4.3	4.2	4.3	6.0	6.8	2.6	1.9	1.9	2.4	2.4
Conductivity, μmhos/cm^2	-	-	-	-	-	-	-	4000	3700	6000	900	1700

TABLE 15 (continued)

	Well locations										
	J6	J6	J6	J7	J7	J7	J7	J7	J7	J7	J7
Depth, m	8.2	11.5	12.8	1.6	4.5	5.0	6.8	7.9	8.8	10	11.2
Strata	Clay-silt	Clay-silt	Clay-silt	Clay-silt	Clay-silt	Clay-silt	Clay-silt and sand	Clay-silt and sand	Clay-silt and sand	Clay-silt and sand	Clay-silt and sand
Alumimum, mg/L	2.5	6.4	9.1	1.15	3.5	2.8	3.6	8.4	8.1	23	11
Barium, mg/L	< 0.1	-	< 0.1	-	< 0.1	1.9	-	< 0.1	1.8	-	2.3
Beryllium, mg/L	-	-	-	-	-	-	-	-	-	-	-
Calcium, mg/L	62	78	130	420	660	510	37	51	58	59.5	73
Cadmium, mg/L	0.006	0.006	-	< 0.001	-	0.002	0.004	-	-	0.005	0.003
Chromium, mg/L	< 0.001	0.015	0.01	< 0.001	< 0.01	0.003	0.005	< 0.01	0.02	0.09	0.021
Copper, mg/L	< 0.1	0.07	< 0.1	0.01	< 0.1	0.3	0.06	0.2	0.2	0.03	< 0.1
Iron, mg/L	38	25	64	1.4	0.8	50	2.7	8.1	5.2	92	85
Magnesium, mg/L	12	-	19	-	63	41	-	20	32	-	15
Mercury, mg/L	< 0.02	< 0.01	< 0.02	< 0.01	< 0.02	< 0.02	-	< 0.02	< 0.02	< 0.01	< 0.01
Nickel, mg/L	< 0.5	< 0.05	< 0.5	0.11	< 0.5	< 0.5	0.09	< 0.05	< 0.05	0.12	< 0.5
Lead, mg/L	0.07	0.018	-	< 0.002	-	0.004	0.016	16	-	0.07	0.035
Selenium, mg/L	< 0.05	< 0.05	-	< 0.02	-	< 0.10	< 0.05	-	-	< 0.05	< 0.05
Sulfate, mg/L	260	-	< 100	-	1500	-	-	100	230	-	-
Zinc, mg/L	0.5	0.53	2.2	0.03	5.0	2.6	0.38	0.9	2.5	0.43	1.7
pH, std. units	7.1	2.3	2.7	7.2	6.8	1.7	1.7	1.5	1.4	2.1	2.2
Conductivity, µmhos/cm²	575	2200	2100	2750	1950	2700	1200	4500	20,000	9500	3550

TABLE 16. ANALYSIS OF EXTRACTED INTERSTITIAL WATER FROM PLANT L

Constituents	Sampling locations L3	L6	L6	L6	L6	L7	L8
Depth, meters	15.0	8.0	8.8	10.0	10.6	8.2	0.9
Strata	Silt-clay	Ash	Ash	Ash	Ash	Silt-clay	Ash
Aluminum, mg/l	2.2	8.4	8.6	2.0	8.2	7.7	4.1
Barium, mg/l	0.400	0.600	0.600	0.500	0.600	0.600	0.200
Beryllium, mg/l	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010
Calcium, mg/l	96	220	280	320	210	200	170
Cadmium, mg/l	0.010	0.080	0.040	0.020	0.010	0.020	0.020
Chromium, mg/l	<0.050	0.110	0.050	<0.050	0.060	<0.050	<0.050
Copper, mg/l	<0.010	0.110	0.090	0.020	0.060	0.070	0.030
Iron, mg/l	1.9	9.5	6.3	8.8	19	8.9	3.5
Mercury, mg/l	<0.004	<0.004	<0.004	<0.004	<0.004	<0.004	<0.004
Magnesium, mg/l	21	3.8	6.3	16	12	14	9.8
Manganese, mg/l	0.140	0.550	0.450	1.6	1.2	3.5	0.580
Nickel, mg/l	<0.050	0.100	0.070	0.120	0.090	0.080	0.090
Lead, mg/l	0.050	0.050	0.050	0.050	0.120	0.100	0.050
Zinc, mg/l	0.070	1.8	0.620	0.690	0.640	0.400	0.330
pH, standard units	7.5	3.5	3.6	6.5	4.1	2.9	3.4
Conductivity, μmhos/cm	880	1180	1130	1040	3000	6400	1650
Alkalinity, mg/l as $CaCO_3$	320	-	-	-	-	-	-
Sulfate, mg/l	100	900	900	920	600	500	860

at plant L was because the compacted nature of the soils precluded the extraction of enough water for laboratory analysis. In Tables 15 and 16, the results of analyses on the interstitial waters from plants J and L, respectively, are presented. The dashes that appear in these tables indicate analyses were not performed because an insufficient amount of extracted water was available to accommodate the analytical evaluation. The minimum detection limits shown for the same elements are also a result of insufficient sample volume.

One of the most striking features about the data in Tables 15 and 16 is the low pH values observed. At plant J, 16 of the 23 pH measurements were less than 5.0, and 13 of the values were below 3.0. At plant L, five of the seven measurements for pH were below 5.0, and one less than 3.0. The data do not, however, indicate any trends in pH, such as with depth or stratum type. In addition, the constituent concentrations in these tables do not always track with variations in pH, as would be expected from solubility relationships. For example, iron concentrations at sampling location J7 (Table 15) are not inversely proportional to pH, and zinc concentrations at location J4 demonstrate similar behavior. The solubilities of the elements in Tables 15 and 16 in relation to other matrices in which they were measured are obviously a factor to consider and this subject is discussed later in the report.

GROUNDWATER ANALYSIS

In Tables 17 and 18, the results of the laboratory analysis performed on groundwater samples collected from the wells at plant J and L, respectively, are presented. Samples were collected from all sampling locations at plant J, except J1, on July 2, 1976, and from all locations except J3 and J3A on March 9, 1977. These sample omissions were a result of sampling well malfunctions. Groundwater samples were collected from all sampling locations at plant L, on February 22, 1977.

For comparative purposes, the EPA's domestic water supply criteria[16] are also listed in Tables 17 and 18. Although these criteria are not applicable to leachate from solid waste disposal sites, they are used here, and elsewhere in this report, as a screening process to identify water quality constituents that may deserve environmental consideration. Of the constituents measured in samples from plant J, five were found to exceed EPA's criteria for iron, manganese, lead, dissolved solids (as sulfate), and pH. Samples from all wells except J1, a background well, exceeded the criterion for iron; samples from all wells in the March collection exceeded the manganese criterion; and the criterion for dissolved solids was exceeded in March at locations J4, J4A, J5A, J7A, and J8. Lead exceeded the criterion in July at locations J6, and the pH was not within the criterion at wells J3, J4, J5B, J6, J6A, and J7.

At plant L, the data indicate that the criterion for iron was exceeded in samples analyzed from wells, L3A, L6A, L7, L8A, and L9A. Dissolved solids, as sulfate, exceeded the criterion in samples from

TABLE 17. ANALYSIS OF GROUNDWATER SAMPLES COLLECTED FROM SAMPLING WELLS AT PLANT J - JULY 2, 1976

Parameter	J2	J3	J3A	J4	J4A	J5	J5A	J6	J6A	J7	J8	DWSC[a]
						July 2, 1976						
Aluminum, mg/L	0.8	2.0	520	5.2	170	2.3	40	2.3	85	7.2	5.4	b
Beryllium, mg/L	< 0.01	< 0.01	0.07	< 0.01	0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	b
Cadmium, mg/L	< 0.001	< 0.001	< 0.001	0.001	< 0.001	< 0.001	< 0.001	0.001	0.003	< 0.001	0.001	0.01
Calcium, mg/L	92	27	280	36	420	100	400	160	85	39	360	b
Chromium, mg/L	< 0.005	< 0.005	< 0.005	0.01	< 0.005	< 0.005	< 0.005	0.006	< 0.005	0.012	0.012	0.05
Copper, mg/L	0.04	0.08	1.4	0.06	0.18	0.04	0.09	0.06	0.07	0.04	0.07	1.0
Iron, mg/L	10	9.3	2000	6.8	680	98	640	12	200	5.6	13	0.3
Lead, mg/L	< 0.01	0.011	0.044	0.043	< 0.01	< 0.01	< 0.01	0.042	0.089	0.011	0.026	0.05
Mercury, mg/L	< 0.0002	< 0.0002	0.0029	< 0.0002	0.0006	< 0.0002	< 0.0002	< 0.0002	< 0.0002	< 0.0002	< 0.0002	0.002
Nickel, mg/L	< 0.05	< 0.05	0.82	< 0.05	0.31	< 0.05	0.18	0.06	0.07	< 0.05	< 0.05	b
Selenium, mg/L	< 0.001	< 0.001	0.005	0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	0.01
Dissolved solids, total, mg/L	450	150	680	210	-	590	8100	530	270	190	1800	250
Zinc, mg/L	0.04	0.09	1.3	0.2	2.1	0.08	0.41	0.05	0.19	0.03	0.08	5.0
pH, standard units	6.6	9.5	8.9	9.5	7.1	8.2	8.1	10	9.2	9.7	8.0	5.9

TABLE 17 (continued)

Parameter	J1	J2	J4	J4A	J5	J5A	J5B	J6	J6A	J7A	J8	DWSC[a]
						March 9, 1977						
Aluminum, mg/L	0.3	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	0.4	< 0.2	< 0.2	< 0.2	< 0.2	b
Arsenic, mg/L	< 0.004	0.026	< 0.004	< 0.004	< 0.004	0.006	< 0.004	< 0.004	< 0.004	< 0.002	< 0.002	0.05
Boron, mg/L	0.16	5.6	0.2	0.26	0.09	0.61	0.13	0.2	0.2	2.0	0.16	b
Barium, mg/L	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	1.0
Beryllium, mg/L	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	b
Calcium, mg/L	62	110	110	410	19	260	18	110	100	520	360	b
Cadmium, mg/L	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	0.01
Chromium, mg/L	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	0.05
Copper, mg/L	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.02	< 0.01	< 0.01	< 0.01	< 0.01	1.0
Iron, mg/L	< 0.05	16	< 0.05	420	0.57	2200	3.7	1.6	77.0	7.0	0.24	0.3
Mercury, mg/L	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	0.002
Magnesium, mg/L	17	42	16	120	12	100	10	15	18	96	70	b
Manganese, mg/L	0.13	4.6	0.64	44	0.24	63	4.5	3.5	7.3	18	2.2	0.05
Nickel, mg/L	< 0.05	< 0.05	< 0.05	0.08	< 0.05	0.06	< 0.05	< 0.05	< 0.05	0.08	< 0.05	b
Lead, mg/L	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.04	< 0.01	< 0.01	< 0.01	< 0.01	0.05
Selenium, mg/L	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	0.01
Sulfate, mg/L	68	65	310	2100	30	3400	130	120	150	1700	890	250
Sulfide, mg/L	0.08	< 0.02	< 0.02	0.07	< 0.02	0.13	< 0.02	< 0.02	< 0.02	0.03	< 0.02	b
Dissolved solids, total, mg/L	410	1400	900	4000	210	4900	390	950	1200	3400	2700	250
Volatile solids, total, mg/L	10	70	40	570	10	500	50	50	70	250	120	b
Zinc, mg/L	< 0.02	< 0.01	< 0.01	< 0.01	< 0.01	0.05	0.2	< 0.01	0.02	0.01	0.02	5.0
pH, standard units	7.5	7.1	6.8	6.6	7.0	6.5	3.3	7.4	6.9	7.0	7.6	5.9
Oxidation reduction potential, MV	+130	-135	-70	-100	-130	-110	+200	-100	-160	-110	+150	b
Conductivity, µmhos/cm^2	470	790	510	2200	180	2900	360	520	680	1900	1460	b
Alkalinity, mg/L as $CaCO_3$	192	390	-	-	81	108	-	237	320	320	295	b
Water table elevation, m	230.48	228.55	224.79	224.03	224.70	223.75	221.16	220.19	224.36	225.13	228.22	b

[a] Domestic Water Supply Criteria, EPA, 1976.

[b] Not analyzed.

TABLE 18. ANALYSIS OF GROUNDWATER SAMPLES COLLECTED FEBRUARY 22, 1977, FROM SAMPLING WELLS AT PLANT L

Parameter	L1	L2	L2A	L3	L3A	L4	L5	L6	L6A	L7	L8	L8A	L9	L9A	L10	L11	DWSC[a]
Aluminum, mg/L	0.8	0.5	< 0.2	0.3	0.2	0.4	< 0.2	< 0.2	< 0.2	2.3	< 0.2	11	< 0.2	< 0.2	< 0.02	< 0.02	b
Arsenic, mg/L	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	-	0.01	-	0.005	< 0.002	0.019	< 0.002	0.035	< 0.002	< 0.002	0.05
Boron, mg/L	0.15	0.35	0.23	0.2	0.21	0.16	0.24	0.44	8.1	0.31	2.3	20	0.76	6.1	0.16	0.08	b
Beryllium, mg/L	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.04	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	b
Calcium, mg/L	55	81	64	64	120	39	50	110	190	100	270	520	120	180	7.3	27	b
Cadmium, mg/L	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	0.01
Chromium, mg/L	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	0.05
Copper, mg/L	< 0.01	< 0.01	0.04	0.04	0.01	0.02	< 0.01	< 0.01	0.02	< 0.01	0.02	0.03	< 0.01	< 0.01	0.04	< 0.01	1.0
Iron, mg/L	< 0.05	< 0.05	< 0.05	0.06	0.34	0.26	0.13	0.23	13	0.44	0.22	[illegible]	< 0.05	0.87	0.08	< 0.05	0.3
Mercury, mg/L	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	0.002
Magnesium, mg/L	4.4	7.1	6.1	15	29	9.0	7.9	25	11	14	40	91	30	20	1.3	12	b
Manganese, mg/L	0.75	0.45	2.9	0.69	1.9	0.47	0.29	0.85	5.6	7.1	2.2	4.7	0.87	1.0	0.22	0.74	0.05
Nickel, mg/L	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	b
Lead, mg/L	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.03	< 0.01	< 0.01	0.05
Selenium, mg/L	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	0.01
Sulfate, mg/L	8.0	10	79	22	39	3.0	10	68	170	8.0	490	2500	21	450	47	13	250
Sulfide, mg/L	0.33	0.04	0.04	0.1	0.2	0.16	0.2	0.44	0.11	0.07	0.16	0.06	0.04	0.16	0.14	0.04	b
Dissolved solids, total, mg/L	190	180	290	180	250	150	150	330	400	450	1000	3700	270	920	160	150	250
Zinc, mg/L	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.02	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.21	< 0.01	< 0.01	< 0.01	0.11	5.0
pH, standard units	7.7	7.8	7.7	8.0	7.9	7.4	8.0	7.4	7.5	8.5	7.2	4.4	7.6	7.5	6.0	7.2	5.9
Oxidation reduction potential, MV	+70	+390	+390	+120	+130	+130	+60	+130	+10	+110	+150	+340	+370	–	+180	+360	b
Conductivity, µmhos/cm²	280	325	530	350	680	280	350	720	930	790	1080	2450	740	250	220	250	b
Alkalinity, mg/L as $CaCO_3$	198	230	246	235	425	132	165	350	416	185	225	-	490	149	57.2	98.5	b
Water table elevation, m	183.21	182.20	185.34	181.41	181.44	182.54	183.02	186.83	186.77	181.03	187.38	189.45	189.06	189.55	180.29	183.51	b

[a] Domestic Water Supply Criteria, EPA, 1976.

[b] Not analyzed.

wells L8, L8A, and L9A. The pH in well L8A was not within the criterion, and manganese exceeded the criterion in all wells sampled, including the background wells.

The data also indicate that pH values measured in samples collected from the sampling wells (Tables 17 and 18) were generally higher than values obtained from the extracted interstitial water samples (Tables 14 and 15). Samples from the wells were generally neutral to alkaline, with only two depressed pH values observed (wells L8A and J5B), while the pH of the interstitial water was generally very acidic (a pH of 1.4 was measured), but ranged to alkaline. Although the methods of collection differ between the interstitial water and the well water, it was possible to compare samples collected by both methods from the same location and depth. These comparisons are given in Table 19, along with the soil core sample concentrations for the same locations and depth. The table shows that in all cases where measurable quantities of a constituent were found the concentration in the interstitial water sample was greater than that found in the well sample. This comparison indicates that the measurement of interstitial water may be a more accurate method of determining groundwater contamination by leachates than utilizing groundwater monitoring wells of the design used in this study. However, more research is needed to economize and standardize this technique. Specific reactions and chemistry of selected constituents in Table 19 are discussed below.

Aluminum

In aqueous systems, aluminum is strongly influenced by its tendency to form soluble complexes with fluoride, hydroxide, sulfate, phosphate, and some organic ligands; its solubility is affected by the concentrations of these ligands.[17] The solubility of aluminum, as a function of pH, in a hydroxide equilibrium environment, is illustrated in Figure 8. On the alkaline side of the curve, the main species present is monovalent $AL(OH)_4^{-1}$, while under acidic conditions the main species is the trivalent form Al^{+3}. However, in aqueous solutions such as the interstitial water in Table 19, other complexing ligands in addition to hydroxide may alter the solubility of aluminum through complexation. For example, the concentration of sulfate in an interstitial water sample collected from location J4 was measured at 2300 mg/l, with a pH of 4.3. Roberson and Hem[18] studied the solubility of aluminum in the presence of different concentrations of sulfate and at different pH's, and Figure 9 illustrates the solubility of microcrystalline gibbsite ($Al(OH)_3$) as a function of sulfate concentrations over the ranges of pH from their studies. Using the data from location J4, at 2300 mg/l sulfate and a pH of 4.3, the relationship presented in Figure 9 indicates that approximately 270 mg/l of aluminum could be soluble in the interstitial water sample. In addition, using values from location J4 at 310 mg/l sulfate and a pH of 6.8 for the well water sample, 0.04 mg/l of soluble aluminum could be present in the well water according

TABLE 19. COMPARISON OF CONCENTRATIONS MEASURED IN GROUNDWATER SAMPLING WELLS, EXTRACTED INTERSTITIAL WATER, AND SOLID SUBSTRATUM MATERIAL, PLANTS J AND L

	Sampling location and site								
	Location J3 (13.4 m)			Location J4 (8.0 m)			Location J5 (8.4 m)		
Constituent	Groundwater sampling wells	Extracted interstitial water	Solid substratum material	Groundwater sampling wells	Extracted interstitial water	Solid substratum material	Groundwater sampling wells	Extracted interstitial water	Solid substratum material
pH, standard units	9.5	7.3	-	6.8	4.3	-	7.0	1.8	-
Alkalinity, mg/L as $CaCO_3$	-	-	-	-	-	-	81	-	-
Oxidation reduction potential, MV	-	-	-	-70	-	-	-130	-	-
Dissolved solids, total, mg/L	150	-	-	900	-	-	210	-	-
Volatile solids, total, mg/L	-	-	-	40	-	-	10	-	-
Aluminum, mg/L	2.0	3.2	2700	< 0.2	60	3900	< 0.2	62	7000
Arsenic, mg/L	-	-	-	< 0.004	-	-	< 0.004	-	-
Boron, mg/L	-	-	-	0.2	-	-	0.09	-	-
Barium, mg/L	-	< 0.1	45	< 0.1	< 0.1	54	< 0.1	-	36
Beryllium, mg/L	< 0.01	-	-	< 0.01	< 0.01	< 1.0	< 0.01	-	< 1.0
Calcium, mg/L	27	56	800	110	350	160	19	310	160
Cadmium, mg/L	< 0.001	-	-	< 0.001	-	< 1.0	< 0.001	0.005	< 1.0
Chromium, mg/L	< 0.005	< 0.01	< 5.0	< 0.005	0.06	< 5.0	< 0.005	0.7	7.0
Copper, mg/L	0.08	0.3	12	< 0.01	0.3	< 1.0	< 0.01	0.27	6.0
Iron, mg/L	9.3	15	3200	< 0.05	1200	3700	0.57	1000	14,000
Mercury, mg/L	< 0.0002	-	< 0.1	< 0.002	< 0.02	-	< 0.002	< 0.01	-
Magnesium, mg/L	-	14	650	16	91	300	12	-	350
Manganese, mg/L	-	-	-	0.64	-	-	0.24	-	-
Nickel, mg/L	< 0.05	< 0.5	< 5.0	< 0.05	0.8	< 5.0	< 0.05	0.5	7.0
Lead, mg/L	0.011	-	10	< 0.01	0.42	7.0	< 0.01	0.017	21
Selenium, mg/L	< 0.001	-	-	< 0.001	-	-	< 0.001	< 0.05	-
Sulfate, mg/L	-	-	< 4.0	310	2300	130	30	-	5600
Sulfide, mg/L	-	-	-	< 0.01	-	-	< 0.02	-	-
Zinc, mg/L	0.09	0.7	19	< 0.01	4.8	12	< 0.01	1.3	17

TABLE 19 (continued)

Constituent	Sampling location and site								
	Location L3 (15.0 m)			Location L6 (10.6 m)			Location L7 (8.8 m)		
	Groundwater sampling wells	Extracted interstitial water	Solid substratum material	Groundwater sampling wells	Extracted interstitial water	Solid substratum material	Groundwater sampling wells	Extracted interstitial water	Solid substratum material
pH, standard units	8.0	7.5	-	7.5	4.1	-	8.5	2.9	-
Alkalinity, mg/L as $CaCO_3$	235	320	-	930	-	-	185	-	-
Oxidation reduction potential, MV	+120	-	-	+10	-	-	+110	-	-
Dissolved solids, total, mg/L	180	-	-	400	-	-	450	-	-
Volatile solids, total, mg/L	-	-	-	-	-	-	-	-	-
Aluminum, mg/L	0.3	2.2	26,000	< 0.2	8.2	22,000	2.3	7.7	18,000
Arsenic, mg/L	< 0.002	-	< 1.0	-	-	< 1.0	0.005	-	< 3.0
Boron, mg/L	0.2	-	-	8.1	-	-	0.31	-	-
Barium, mg/L	-	0.4	110	-	0.6	90	-	0.6	160
Beryllium, mg/L	< 0.01	< 0.01	3.0	< 0.01	< 0.01	1.0	< 0.01	< 0.01	2.0
Calcium, mg/L	64	96	4600	190	210	1400	100	200	8000
Cadmium, mg/L	< 0.001	0.01	< 1.0	< 0.001	0.01	< 1.0	< 0.001	0.02	< 1.0
Chromium, mg/L	< 0.005	< 0.05	48	< 0.005	0.06	36	< 0.005	< 0.05	28
Copper, mg/L	0.04	< 0.01	32	0.02	0.06	9.0	< 0.01	0.07	14
Iron, mg/L	0.06	1.9	49,000	13	19	40,000	0.44	8.9	36,000
Mercury, mg/L	< 0.002	< 0.004	0.1	< 0.002	< 0.004	0.1	< 0.002	< 0.004	0.1
Magnesium, mg/L	15	21	12,000	11	12	980	14	14	6500
Manganese, mg/L	0.69	0.14	-	5.6	1.2	-	7.1	3.5	-
Nickel, mg/L	< 0.05	< 0.05	97	< 0.05	0.09	11	< 0.05	0.08	37
Lead, mg/L	< 0.01	< 0.05	41	< 0.01	0.12	17	< 0.01	0.1	37
Selenium, mg/L	< 0.001	-	< 1.0	< 0.001	-	< 1.0	< 0.001	-	< 1.0
Sulfate, mg/L	22	100	28	170	600	34	8.0	-	28
Sulfide, mg/L	0.1	-	-	0.11	-	-	0.07	-	-
Zinc, mg/L	< 0.01	0.07	90	< 0.01	0.64	47	< 0.01	0.4	85

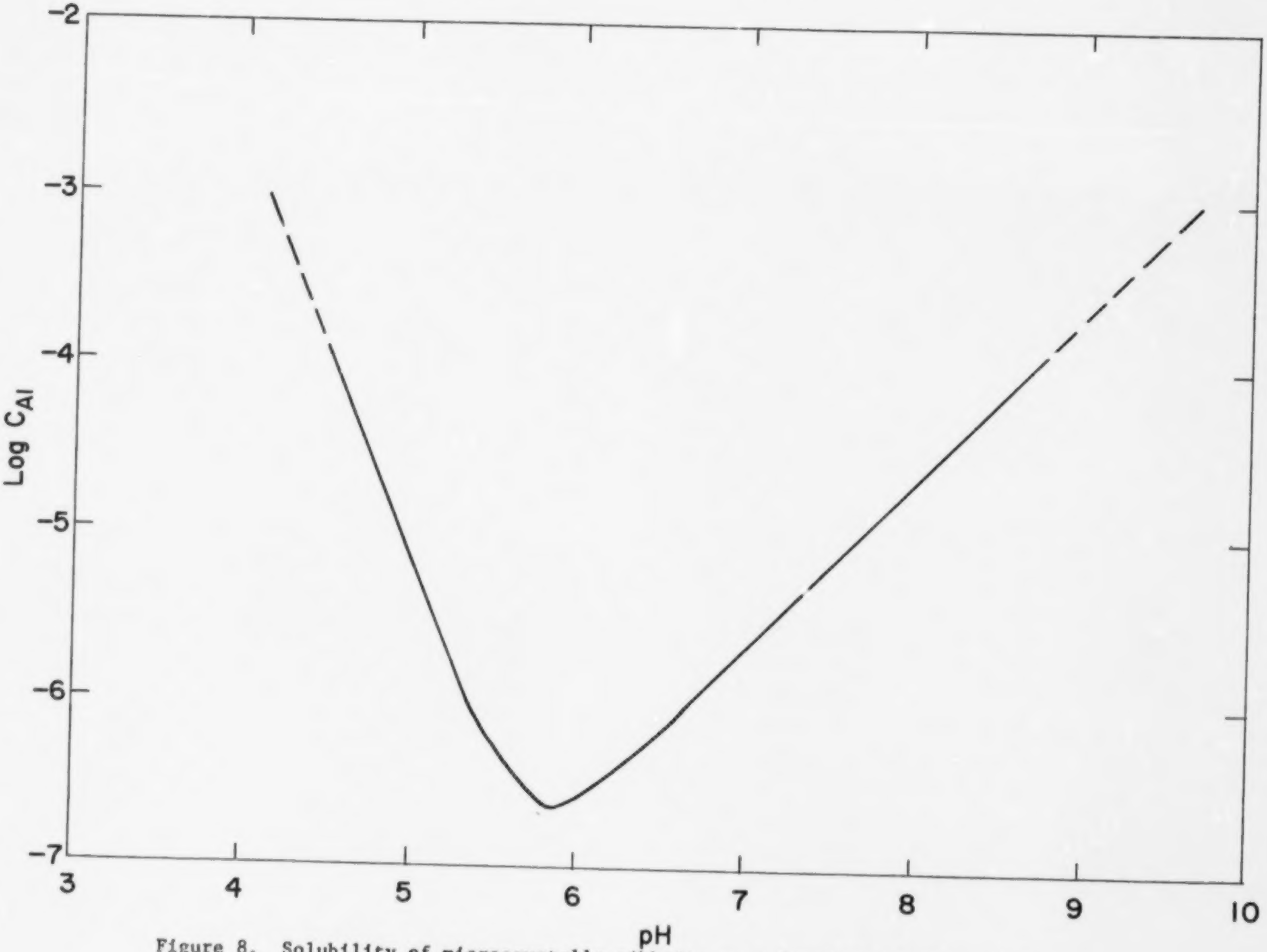

Figure 8. Solubility of microcrystalle gibbsite as a function of pH, at 25° C., and 1 atmosphere total pressure (from Roberson and Hem, 1969).

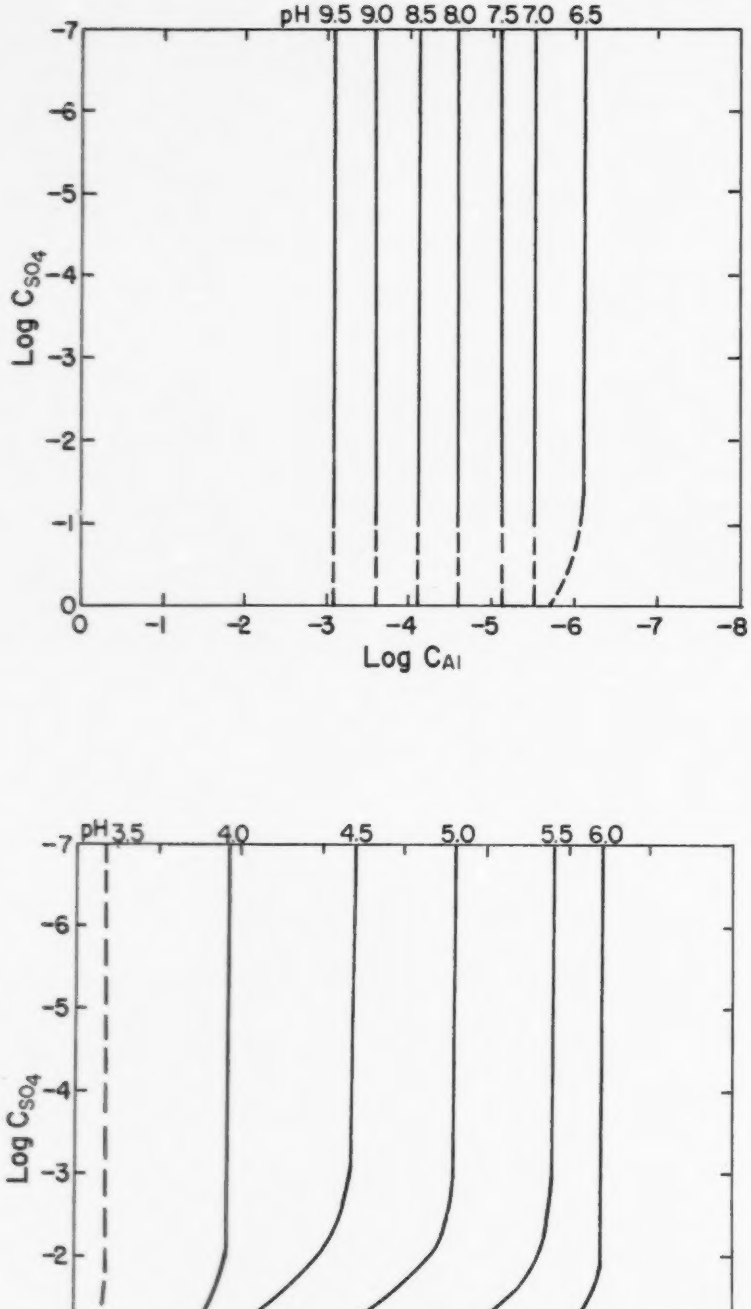

Figure 9. Solubility of microcrystalline gibbsite as a function of sulfate concentration. Ionic strength 0.10 for 25°C, and 1 atmosphere total pressure (from Roberson and Hem, 1969).

to the relationship expressed in Figure 9. From Table 19, the concentrations of aluminum actually measured in the interstitial and well water samples at location J4, are 60 and <0.20 mg/l respectively. The concentration of aluminum in the well water sample may agree with the value predicted from Figure 9, but it cannot be verified because the detectable limit is higher than the predicted value. The concentration of aluminum in the interstitial water sample (60 mg/l), however, is 4.5 times less than the predicted value (270 mg/l). It might be postulated that 60 mg/l was all the aluminum available for solubilization; however, a return to Table 19, location J4, shows that 3900 µg/g of aluminum was present in the (soil) substratum. The soil moisture content was approximately 20 percent (see Table 3), and if all the aluminum were to dissolve, calculations indicate that a 624 mg/l aluminum solution would result--more than enough to meet the predicted value.

Thus, it appears that other factors besides the sulfate concentrations affected the solubility of aluminum in the interstitial water samples from location J4. The type of matrix in which the aluminum is chemically bound, incomplete soil-water contact, and competition with other metal ions for the sulfate ligand are factors which might affect aluminum solubility. Further analysis of the data indicates that competition for the sulfate ligand may indeed be the limiting factor. The competition for the sulfate ligand by other metal ions, such as magnesium, calcium, barium, and lead, may force the hydroxide solubility to be limiting for aluminum. The following calculations tend to verify this point:

$$\{Al^{+3}\}\{OH^{-1}\}^3 = K_{so} = 10^{-32} \tag{1}$$

$$\{H^+\}\{OH^-\} = 10^{-14} \tag{2}$$

$$\{Al^{+3}\}_{apparent} = 2.2 \times 10^{-3} \text{ moles/liter} \tag{3}$$

$$pH = -\log \{H^+\} = 4.3 \tag{4}$$

$$\{OH^-\} = 10^{-14}/\{H^+\} \tag{5}$$

$$\{OH^-\} = 10^{-14}/5.0 \times 10^{-5}$$

$$\{OH^-\}_{apparent} = 1.99 \times 10^{-10}$$

Substitution of 3 and 5 into 1 yields:

$$\{Al^{+3}\}_{apparent}\ \{OH^-\}^3_{apparent} = 1.7 \times 10^{-32} \tag{6}$$

The calculated solubility (6), using the measured values of aluminum and pH from Table 19, is close to the theoretical solubility constant (1). These data suggest that the system is in equilibrium and it is the hydroxide solubility that is controlling the aluminum concentration in the interstitial water and, as stated earlier, the predominate form at a pH of 4.3 would be Al^{+3}.

It should be pointed out that the characteristics of the samples from location J4 are not necessarily indicative of all locations at plant J or L. For example, at location J3 (Table 19), the aluminum concentration in both the interstitial water and well water exceeds its hydroxide solubility ($K_{apparent} = 9.4 \times 10^{-25}$ and $K_{apparent} = 2.3 \times 10^{-18}$ respectively) indicating either the occurrence of complexation or the presence of a system not in equilibrium, while for location L6, calculations indicate the concentration of aluminum in the interstitial water has not reached the limit imposed by the hydroxide solubility constant ($K_{apparent} = 6.0 \times 10^{-34}$), even though the concentration is higher than at location J3. This suggests that the acidic conditions (pH 4.1) at location L6 are allowing more aluminum in solution, but not enough is present to attain maximum equilibrium concentrations.

It should be noted that the simplistic approach used in the equilibrium discussions herein minimizes the effects of ionic strength, temperature, and medium on K_{so}.

Iron

There are two oxidation states in which iron normally occurs, the ferrous form (Fe^{+2}), and the ferric form (Fe^{+3}). Under oxidizing conditions and near neutral pH (5 to 8), iron is precipitated as the highly insoluble ($K_{so} = 6.0 \times 10^{-38}$) ferric hydroxide, $Fe(OH)_3$. The solubility of iron is dependent on pH and oxidation-reduction potential (Eh). Its chemical behavior is also influenced by its ability to form complex ions with sulfides, sulfates, oxides, hydroxides, chlorides, fluorides, carbonates, phosphates, and organic material. The ferrous form (Fe^{+3}) forms weaker complexes than the ferric, and forms few stable inorganic complexes. It is the predominate oxidation state in reducing and/or acidic environments.[19]

Figure 10 illustrates the relationships between pH and Eh that define the conditions under which specific ionic species of iron dominate. This is known as an Eh-pH, or stability field, diagram. Specific areas where species dominate are delineated by thermodynamic computations, in which the Nernst equation is the fundamental relationship that establishes the dividing line between oxidized and reduced species. A thorough discussion of Eh-pH diagrams is given by Garrels,[20] where this familiar form of the Nernst equation is utilized.

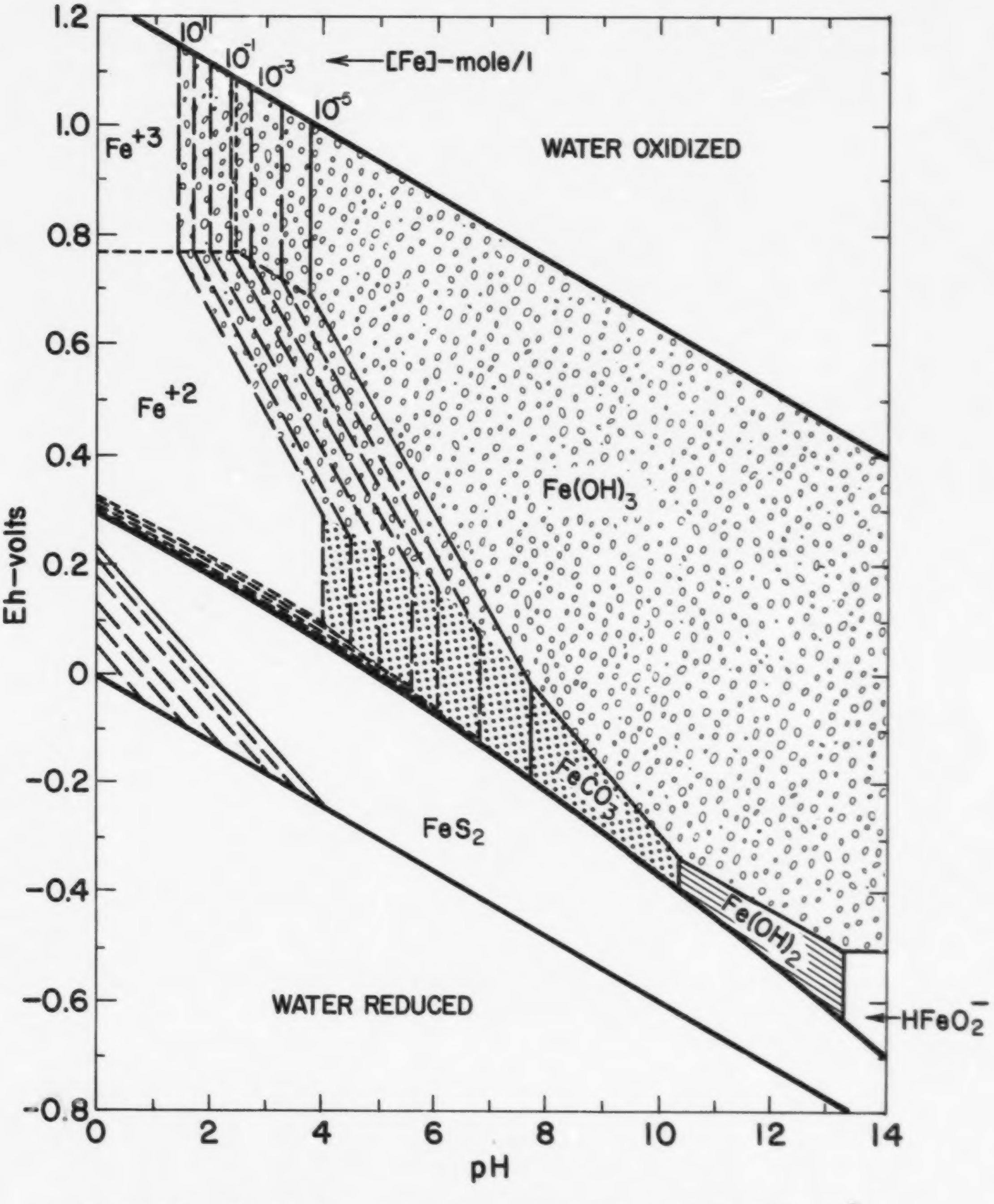

Figure 10. Solubility of iron in relation to pH and Eh at 25° C., and 1 atm. Total dissolved sulfur 10^{-4} M: bicarbonate species 10^{-2} M (Hem, 1969) ⑦

$$Eh = E^{o} + \frac{RT}{nF} \ln \{\frac{ox}{red}\}$$

Where:

Eh = oxidation reduction potential

E^{o} = standard oxidation potential for half-cell reaction

R = universal gas constant (1.987 calories/degree mole)

T = temperature in degrees Kelvin

n = number of electrons involved in chemical reaction

F = Faraday constant (96,484 coulombs)

{ox} = activity of oxidized ions

{red} = activity of reduced ions

This equation can be used with thermodynamic data to generate the stability field diagrams of the type illustrated in Figure 10, for any of the various metal equilibriums one would care to examine. They were not presented for all the metal ions measured during this study because the variable nature of the data, both between and within sampling locations, would require a voluminous exposition.

As Figure 10 indicates, ferrous iron (Fe^{+2}) can be produced by the oxidation of pyrite (FeS_2), reduction of ferric species (Fe^{+3}), dissolution of ferrous hydroxide ($Fe(OH)_2$), or dissolution of siderite ($FeCO_3$). Additionally, the kinetics and formation of intermediate species may affect the formation of ferrous iron. The FeS_2 equilibrium is a feasible condition because of the high concentration of sulfate present in several of the sampling wells, the low pH values of the interstitial water, and the presence of pyrite (FeS_2) in coal. In Figure 11, the stability fields for five different sulfur species are illustrated. The dotted line indicates the ferrous-ferric boundary and demonstrates that sulfate is the predominate form of sulfur stable in the ferric region.

At a pH less than about 8.0, and under reducing conditions, the H_2S and S^{o} forms predominate. Oxidation of H_2S will produce the S^{o} form, which upon further oxidation, forms SO_4^{-2}. The H_2S form has the notorious "rotten egg" odor, which was noticeable during the collection of water samples from several of the wells at both plants. This qualitative analysis indicates the potential presence of a reducing environment in the ground water at certain sampling locations. It was most noticeable in samples collected from wells downgradient from the ash disposal areas, and least, if at all, in the upgradient or background wells. In addition, the odoriferous wells upon inspection were found to have a black deposit (possibly FeS) on the 1.27 cm rigid PVC pipe installed inside the well. This deposit was most concentrated at the interface of the groundwater surface with the atmosphere and may be a result of

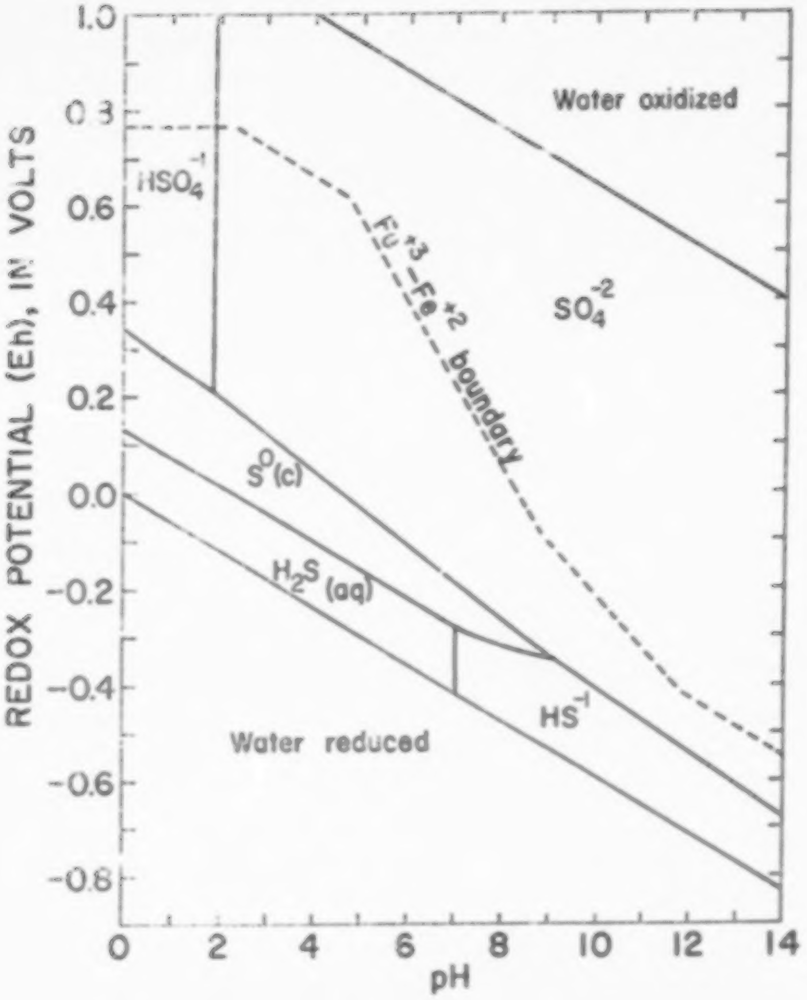

Figure 11. Fields of stability of sulfur species likely to occur in natural water (Hem, 1960) ②

oxidation within the well casing. Solubility product calculations were performed for the FeS, $K_{so} = 2.6 \times 10^{-22}$ equilibrium, using iron and sulfide data from Tables 17 and 18. The calculations indicated that concentrations of iron and sulfide in samples from three locations at plant J (J5A, J4A, and J7A) exceeded the solubility product for FeS, and at plant L, wells L3, L3A, L4, L5, L6, L6A, L7, L8, L8A, L9A, and L10 exceeded the FeS solubility. The water sampled from these wells was thus unstable (not at equilibrium) with regard to the ferrous sulfide equilibrium, and precipitation of FeS could be expected, which may account for the black deposits on the aforementioned PVC pipe.

A potentially important aspect of the speciation chemistry of iron-sulfate equilibrium, as it relates to coal-ash leachate, is the oxidation of pyrite present in the ash disposal area. In a study by Cox, et al,[21] to characterize the runoff from coal storage piles, the production of ferrous iron and acidity from pyrite oxidation was shown to be the major factor effectuating the solubilization of iron. The oxidation of pyrite results in the production of ferrous iron and acidity via the following reactions:

$$2\ FeS_2 + 7O_2 + 2\ H_2O \rightarrow 2\ Fe^{+2} + 4H^+ + 4\ SO_4^{-2} \qquad (1)$$

$$4\ Fe^{+2} + O_2 + 4H^+ \rightarrow 4\ Fe^{+3} + 2H_2O \qquad (2)$$

At this stage the ferric iron can either hydrolyze to form insoluble ferric hydroxide,

$$Fe^{+3} + 3\ H_2O \rightarrow Fe(OH)_3 + 3H^+, \qquad (3)$$

or oxidize pyrite directly producing more ferrous iron and acidity:

$$FeS_2 + 14\ Fe^{+3} + 8\ H_2O \rightarrow 15\ Fe^{+2} + 2\ SO_4^{-2} + 16\ H^+ \qquad (4)$$

The speciation chemistry of the iron-sulfate equilibrium is a complex process, and may be worthy of further study in relation to ash pond leachate due to its potential for decreasing pH and subsequent solubilization of trace metals.

Copper, Lead, Zinc, and Other Metals

At pH values below 7.3, the predominate form of soluble copper is Cu^{+2}, while at higher values $CuOH^+$ is most prevalent. Copper is strongly complexed with inorganic ligands such as carbonates, hydroxides, and chlorides and with organic matter. The low pH values observed in the interstitial water samples indicate the Cu^{+2} form would prevail, while at the higher pH values in the well samples it would precipitate as $Cu(OH)_2$ or $Cu_2(OH)_2CO_3$. In solution at the higher pH values, it could be in the form of $Cu(OH)_4^{=}$, or $CuO_2^{=}$.

Solubility calculations were performed for the copper equilibriums CuS, $CuCO_3$, and $Cu(OH)_2$ using data in Tables 17 and 18 and the stability constants listed in Table 20. The calculations indicated that all well water samples that contained measurable amounts of copper and sulfide were unstable (nonequilibrium) with regard to Cu^{+2}. The solubility limiting equilibrium was found to be CuS as the following calculation, using the data from location L6A, demonstrates:

$\{Cu^{+2}\}$ = 0.02 mg/l = 3.1×10^{-7} mole/liter

$\{S^{=}\}$ = 0.11 mg/l = 3.4×10^{-6} mole/liter

$\{CO_3^{=}\}$ = 1.62 mg/l = 2.7×10^{-5} mole/liter

$\{OH^{-}\}$ = 3.1×10^{-7} mole/liter

Sulfide solubility:

$\{Cu^{+2}\}\{S^{=}\} = 1.0 \times 10^{-12}$ exceeds solubility product, system unstable, precipitation occurring

Hydroxide solubility:

$\{Cu^{+2}\}\{OH^{-}\}^2 = 2.9 \times 10^{-20}$ equal to solubility product, system stable, in equilibruim

Carbonate solubility:

$\{Cu^{+2}\}\{CO_3^{=}\} = 8.3 \times 10^{-12}$ less than solubility product, system unstable, available Cu^{+2}

The calculations indicate that the water sample from L6A is in equilibrium with regard to $Cu(OH)_2$ and not at equilibrium with regard to $CuCO_3$. Above a pH of approximately 7.5 such as at many of the sampling locations at plants J and L, the $Cu(OH)_2$ solubility is exceeded and precipitation occurs.

In waters with pH values below 6.0, the predominate ionic species of lead is the divalent Pb^{+2} form. The solubility of lead can be influenced by complexation with hydroxides, chlorides, and organic material.

In association with sulfates, carbonates, or phosphate anions under alkaline conditions, soluble compounds will readily be formed resulting in the precipitation of lead. Solubility calculations for the PbS equilibrium, $K_{so} = 7.0 \times 10^{-29}$, using data from Tables 17 and 18, indicate that the water sample collected from sampling well L9A at plant L is chemically unstable with regard to the PbS equilibrium, $K_{apparent} = 7.2 \times 10^{-13}$, and precipitation is occurring.

Where:

K_{so} = solubility product at equilibrium

$K_{apparent}$ = solubility product of the measured solution

TABLE 20. SOLUBILITY PRODUCT CONSTANTS FOR IRON, ALUMINUM, COPPER, LEAD, AND ZINC COMPOUNDS

Compound	Solubility product[a]
FeS	2.6×10^{-22}
$Fe(OH)_2$	5.0×10^{-15}
$Fe(OH)_3$	6.0×10^{-38}
$FeCO_3$	2.0×10^{-11}
$Al(OH)_3$	1.0×10^{-32}
Cus	7.9×10^{-37}
$Cu(OH)_2$	1.5×10^{-20}
$CuCO_3$	2.3×10^{-10}
PbS	7.0×10^{-29}
$Pb(OH)_2$	1.5×10^{-17}
$PbCO_3$	7.2×10^{-14}
ZnS	7.9×10^{-26}
$Zn(OH)_2$	5.0×10^{-17}
$ZnCO_3$	2.0×10^{-11}

[a] Adapted from: Sillen, L. G., and A. E. Martell, "Stability Constants of Metal-Ion Complexes." London: The Chemical Society, Burlington House, W. E. (1964).

Generally, the dominating ionic zinc species in solutions of low pH (<7.0) is Zn^{+2}, with the anionic forms $Zn(OH)_3^{-1}$ and $Zn(OH)_4^{-2}$ being the soluble species at high pH (11.0).[23] The carbonate is the most soluble form, $K_{so} = 2.0 \times 10^{-11}$, with the hydroxide following at $K_{so} = 5.0 \times 10^{-17}$. The least soluble zinc compound is the ZnS form with $K_{so} = 7.9 \times 10^{-26}$. Solubility calculations, again using the data in Tables 17 and 18, indicate that in the well samples where measurable zinc and sulfide concentrations were found (L4, L8A, L11, J5A, and J7A), unstable conditions ($K_{apparent} > K_{so}$) with regard to zinc solubility were present, and precipitation was occurring. With measured pH values less than 11, no hydroxo-zinc complexing would be expected; thus, any dissolved zinc species measured in the sampling wells would be predominately the divalent Zn^{+2}.

The concentrations of beryllium, cadmium, chromium, mercury, and selenium measured in the sampling wells at plants J and L, as Tables 17 and 18 indicate, were all less than or near their analytical detection limits. This contrasts with interstitial water analysis in Tables 15 and 16, where concentrations of cadmium, chromium, and mercury were present in measurable quantities.

Arsenic was present in measurable quantities in samples collected from wells J2, J5A, L6, L7, L8A, and L9A. Boron was present in all well samples collected from plants J and L, on March 9 and February 22, respectively. In addition, the concentration of boron in samples from wells J2, J7A, L6A, L8, L8A, L9, and L9A were found to exceed the EPA's quality criteria for water[16] of 0.750 mg/l for irrigation (at one location, L8A, by more than 26 times).

As a result of the comparisons between the data listed in Tables 15, 16, 17, 18, and 19, the solubility calculations that were made using these data, and observations made from the selected Eh-pH diagrams, several trends have become apparent. First, in general these data indicate that the concentrations of metals in the interstitial water samples were higher than concentrations measured for the same constituents in samples taken from the sampling wells; second, interstitial water samples tended to have lower pH values than well samples, perhaps indicating a more reducing environment in the former; third, the predominate form of iron, copper, zinc, and lead ions present in solution was as the divalent species, while aluminum was in the trivalent form; and fourth, the metal-sulfide equilibrium played a dominant role in controlling the solubility of metals (with the exception of aluminum, which was limited by the hydroxide solubility due to its +3 valence state).

SECTION 7

HYDROLOGY

The ash disposal areas at plants J and L are located adjacent to reservoirs in which the water levels in winter are drawn down several feet for flood control. As a result, groundwater discharge to the river is greatest during this period. During the late spring and summer months the reservoir levels are higher, with minor daily variations in elevation. The higher reservoir levels during this time reduce the water table gradient toward the river, resulting in a decreased rate of groundwater discharge to the reservoir.

Although seasonal variations in groundwater flow beneath the ash disposal areas at both plants occur, the net groundwater movement is to the adjacent reservoir. In Figures 12 and 13, water table elevations in the sampling wells at plants J and L, measured respectively on March 9 and February 22, 1977, are plotted along with the average elevation of the associated reservoir levels observed in 1977 (far right horizontal axis). The sampling locations are plotted on the graph from left to right in order of decreasing distance from the river. An estimated line of best fit through the points (dashed line) indicates a riverward gradient and thus, the net direction of groundwater flow at the two disposal areas is toward the river.

Figure 14, is a geologic section and water table profile of the ash pond area at plant J, showing the water table gradient toward the river. The figure also shows a condition that may be common to ash disposal areas where the perimeter dike is constructed of a low permeable material. Subsurface water might be impounded behind the closed perimeter dike continuous with the pond's bottom, both of low permeability (which is the current design). After raising the dike several times to accommodate additional ash, a large bowl with low permeability sides would result. Water in the bottom of this bowl would tend to be passed around by ambient groundwater flows and mixing would be minimal. Static water in this zone would undoubtedly be of poorer quality than water merely passing through coal ash once, acquiring some characteristics of ash leachate, and then flowing on to mix with unaffected ground or surface waters or acted on by attenuation dynamics of the surrounding subsoils. The water in the dead space of the bowl would have a prolonged ash contact time, allowing for maximum dissolution of ions and the formation

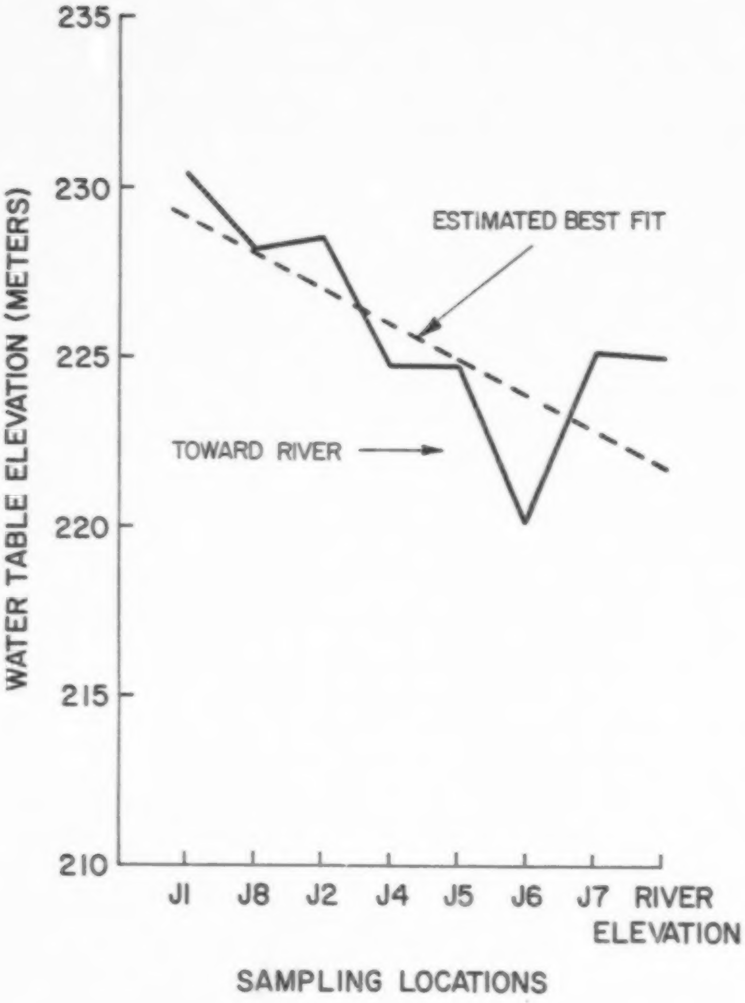

Figure 12. Groundwater table elevation in sampling wells at plant J, March 9, 1977

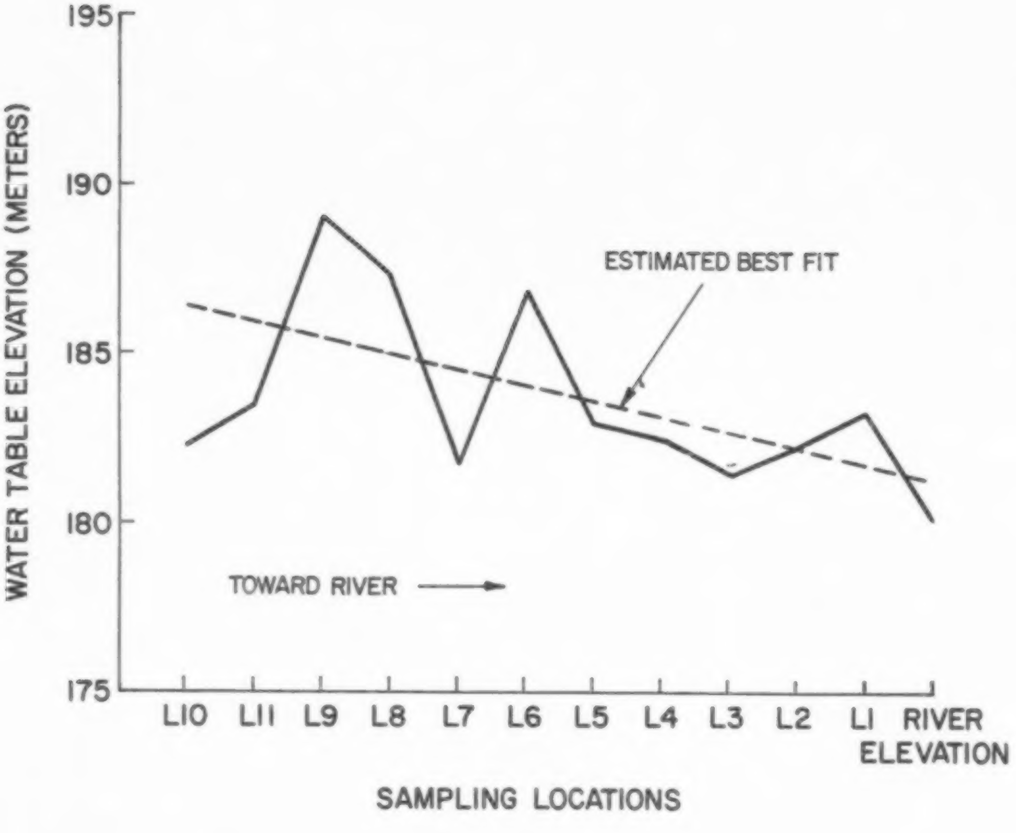

Figure 13. Groundwater table elevation in sampling wells at plant L, February 22, 1977

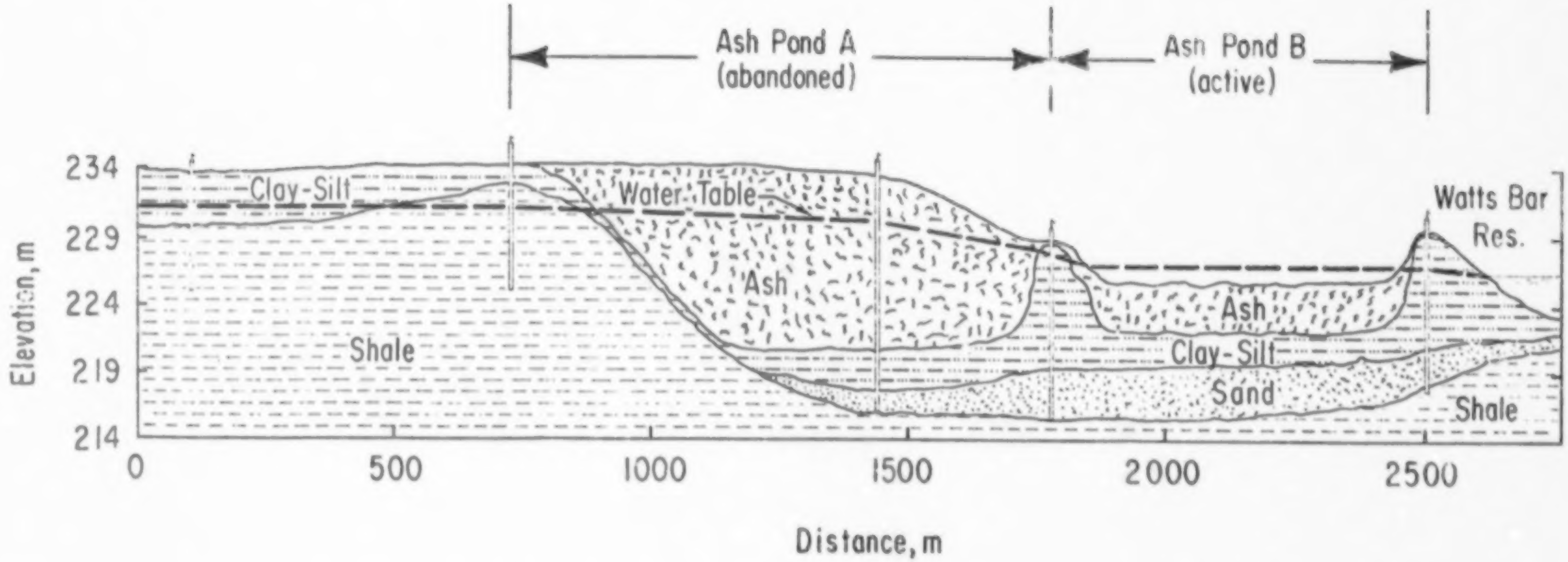
Ash Pond A
(abandoned)
Ash Pond B
(active)
Clay-Silt
Water Table
Ash
Shale
Watts Bar
Res.
Ash
Clay-Silt
Sand
Shale
234
229
224
219
214
Elevation, m
0
500
1000
1500
2000
2500
Distance, m

Figure 14. Cross section of ash disposal area at plant J.

of an acidic, highly reducing environment. The potential impact of a hidden condition such as this on local groundwater quality may warrant determination of whether the phenomenon exists.

In Figure 13, the water table elevations in the abandoned ash ponds at plant L (locations L8 and L9), are higher than the surrounding water table elevations, including the background locations. This is the type of data that would indicate a leachate bowl. Inflows into the bowl would not be able to equilibrate with the surrounding water table if the bowl's sides and bottom were of low permeability (permeability of the soil below the deposited ash at locations L8 and L9, averages 10^{-8} cm/sec), and the water level inside the bowl would tend to rise above the ambient groundwater table. The phenomena is speculative at this point; more data would be required for confirmation.

The permeability of the ash pond dike and subsoil beneath the ash at plant J, was measured in the laboratory in both the vertical and horizontal directions. The vertical permeabilities ranged from 6.3×10^{-8} to 1.3×10^{-6} cm/sec (see Table 3), while horizontal permeabilities ranged from 7.4×10^{-8} to 7.4×10^{-5} cm/sec. Subsoil samples with lower permeabilities contained larger fractions of clay,* while samples with higher permeabilities contained larger fractions of sand (Table 3). The density of the soils ranged from 1.42 to 1.79 g/cm^3. Sample density increased with sand content. Moisture content of plant J soils ranged from 13.9 to 25.7 percent. Generally, the soil samples from plant J, consisting mostly of sand with a moderate moisture content, were of moderate permeability and medium to high density.

At plant L, vertical permeabilities ranged from 6.9×10^{-9} to 3.0×10^{-4} cm/sec, and horizontal permeabilities ranged from 5.7×10^{-9} to 1.5×10^{-4} cm/sec (see Table 7). The sample with 10^{-4} cm/sec permeability was an ash sample collected at location L8. In general, soil samples from plant L having the lowest permeability also contained a large percentage of clay, while the higher permeable samples contained more sand (with the exception of L8, which was ash at 0.8 meters). The densities of the soil material at plant L ranged from 1.03 to 1.77 g/cm^3; moisture ranged from 17.5 to 57.5 percent. Soil samples from plant L, consisting mostly of highly compacted silty clay, were generally of low permeability and high moisture content.

Figure 15 shows an idealized cross section of the ash pond dike at plant J; the superimposed values are mean horizontal permeabilities (K) as measured on samples of the clay-silt and sand strata collected at locations J4, J5, and J6. The permeabilities of both strata were

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*Textural classification of soil fractions as per American Society for Testing and Materials designation, where: clay <0.005 mm, silt 0.005 to 0.074 mm, sand 0.074 to 4.75 mm, and gravel >4.75.[24]

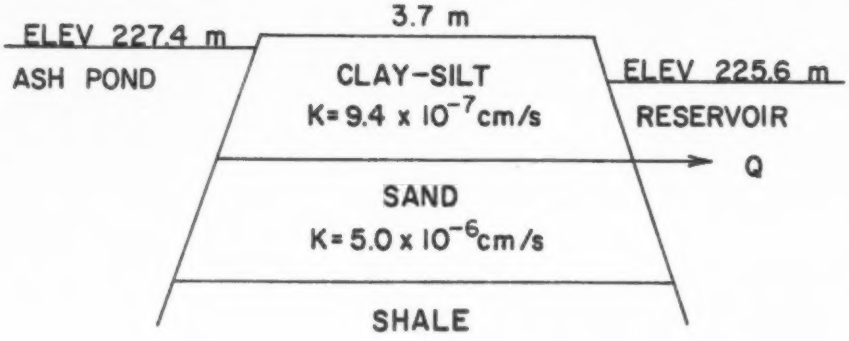

3.7 m
ELEV 227.4 m
ASH POND
CLAY-SILT
K= 9.4 x 10⁻⁷ cm/s
ELEV 225.6 m
RESERVOIR
Q
SAND
K= 5.0 x 10⁻⁶ cm/s
SHALE

Figure 15. Cross section of the clay-silt and sand strata at plant J, showing mean horizontal permeabilities (K) for locations J4, J5, and J6.

very low, with the permeability of clay-silt stratum being the lower of the two. Using a modification of Darcy's law, the flow through a discrete saturated substratum, such as the clay-silt substratum, is:

$$Q = TIW \tag{5}$$

Where: T = coefficient of transmissibility, volume per unit time per unit length of stratum width

I = hydraulic gradient, unitless

W = width of the vertical section through which the flow occurs, unit length

and,

$$T = Km \tag{6}$$

Where: K = average coefficient of permeability from top to bottom of stratum, volume per unit time

m = thickness of stratum, unit length

For example, in the clay-silt stratum at locations J4, J5, and J6, the average horizontal coefficient of permeability (from Table 3) was 9.4×10^{-7} cm/sec, and the average thickness of the stratum was 9.8 meters. Conversion of the coefficient of permeability to liters per day gives 0.83 liters per day, per square meter. Substitution into equation 6 produces a coefficient of transmissibility of 7.9 liters per meter of stratum width for the clay-silt stratum. The width of the vertical section through which the flow occurs (W) corresponds to the linear length of the ash pond dike adjacent to the reservoir, and was measured to be approximately 1718 meters. The hydraulic gradient (I) of the water table was 0.5. Substituting into equation 5:

$$Q = (7.95 \ \frac{\text{liters}}{\text{day-m}})(0.5)(1718 \text{ m})$$

$$Q = 6824 \text{ liters per day (1803 gallons per day)}$$

gives the total groundwater flow passing through this cross-sectional area of the clay-silt stratum. A similar calculation for the sand stratum, where the average permeability was 5.0×10^{-6} cm/sec and the average stratum thickness for locations J4, J5, and J6 was 2.5 meters, indicates a total flow through this stratum of 9265 liters per day. Combining the flows through the clay-silt and sand strata gives a total flow through both strata of 16,090 liters per day. This compares to a surface discharge from the ash disposal pond at plant J, of from 59.4

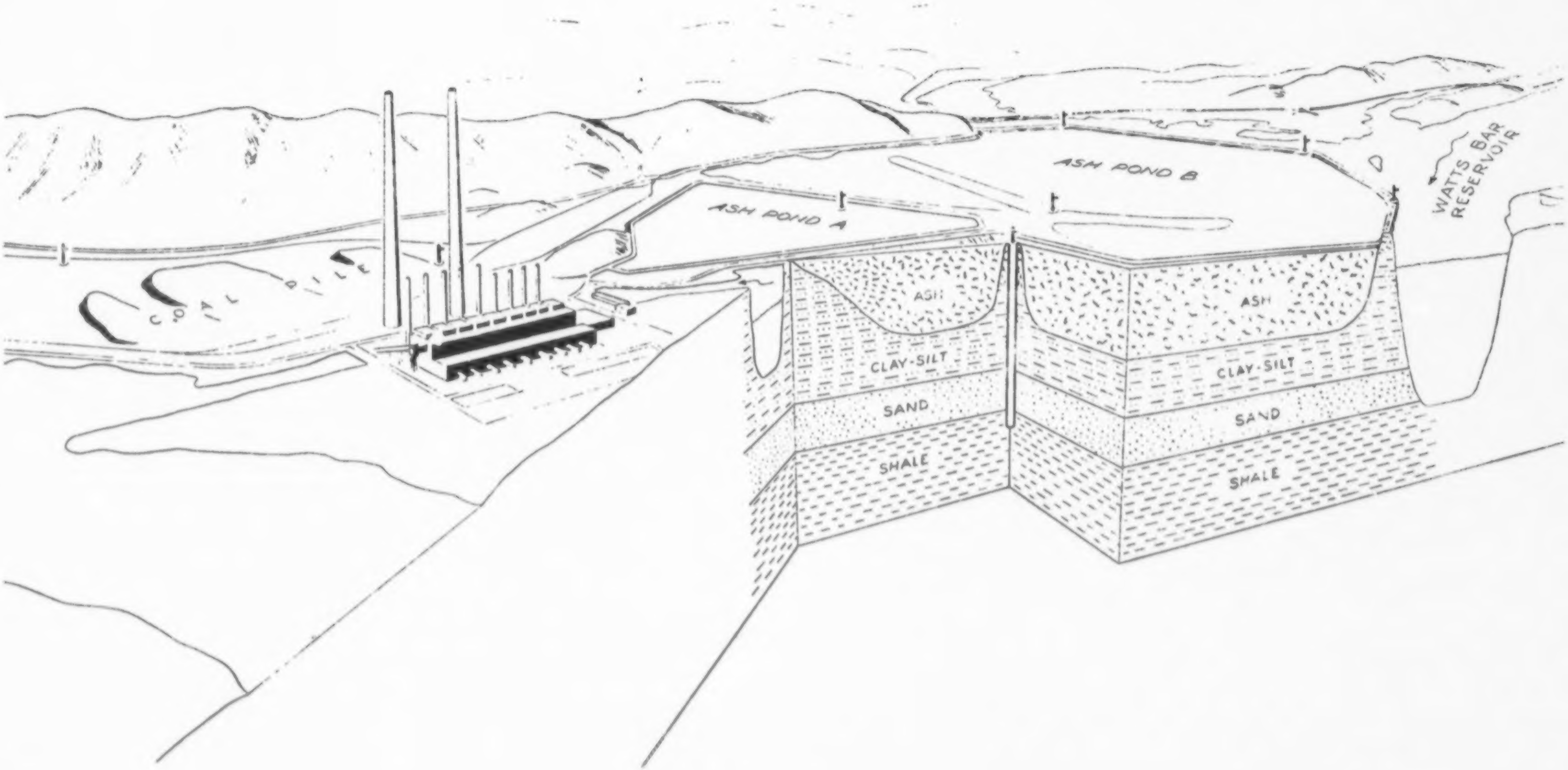

COAL PILE
ASH POND A
ASH POND B
WATTS BAR RESERVOIR
ASH
CLAY-SILT
SAND
SHALE
ASH
CLAY-SILT
SAND
SHALE

Figure 16. Cross section of substratum below plant J's ash disposal area.

TABLE 21. FLUX OF SELECTED CONSTITUENTS THROUGH SUBSTRATA AT PLANT J

Constituent	Concentration in clay-silt mg/l	Clay-silt flux g/24 hr.	Concentration in sand mg/l	Sand flux g/24 hr.	Total ground water flux g/24 hr.	Concentration in ash pond discharge mg/l	Ash pond discharge flux g/24 hr.
Aluminum	98	671	3.2	30	701	1.4	142,088
Calcium	301	2054	98	914	2968	22.5	2,283,567
Cadmium	<0.002	0.013	0.001	9.26	9.27	0.0015	152
Chromium	<0.005	0.034	0.007	0.064	0.098	<0.005	-
Copper	0.113	0.773	0.053	0.494	1.26	0.06	6089
Iron	506	3457	38.9	360	3817	2.35	238,505
Magnesium	79.3	541	14.3	132	673	3.1	314,624
Nickel	0.18	1.27	0.05	0.494	1.76	<0.05	-
Lead	0.036	0.247	0.032	0.293	0.540	<0.01	-
Sulfate	1883	12,851	153	1420	14,271	88.5	8,982,033
Zinc	0.90	6.14	0.110	1.02	7.16	0.05	5074

to 16.2 million liters per day during 1976. It should be noted that the flow (Q) is dependent on the hydraulic gradient (I), while transmissibility (T) and width (W) remain constant. The hydraulic gradient fluctuates with time according to the elevation of the adjacent reservoir, subsequently increasing or decreasing subsurface discharge.

Figure 16 shows a cross section of the ash pond and substrata at plant J and illustrates the spatial relationships between the ash, clay-silt, sand, and shale materials. The total flux of aluminum, calcium, cadmium, chromium, copper, iron, magnesium, nickel, lead, sulfate, and zinc were calculated for the combined flows in the clay-silt and sand strata illustrated in Figure 16 (detailed vertical profiles of the substratum at plants J and L are presented in appendix B). These fluxes are compared (see Table 21) to the total mass of the same constituents discharged from the ash pond's surface effluent. The fluxes in the groundwater were obtained by averaging the concentrations measured (Table 17) at locations J4A, J5A, and J6A for the clay-silt flux, and J4, J5, and J6, for the sand flux. The product of the average concentrations and the clay-silt and sand flows calculated above, gives the 24-hour flux in each strata. The summation of these two fluxes provides the total groundwater flux of each constituent. These calculations were made assuming concentration homogeneity within each stratum, and disregarding attenuation processes. The mass constituent discharged from the ash pond via the surface effluent was determined by averaging the concentrations measured in two samples collected during 1976, and multiplying this value by the average 1976 daily effluent discharge.

Comparison of the columns in Table 21 shows that the total flux of aluminum, calcium, copper, iron, magnesium, nickel, and zinc was greatest in the clay-silt stratum, while in the sand stratum cadmium, chromium, lead, and sulfate flux were greatest. Comparison of the total flux through both strata with the total mass from the ash pond surface discharge shows that the flux through both strata combined was a small percentage (less than 1 percent) of the total mass discharged from the ash pond surface effluent. Albeit, with the exception of copper, constituent concentrations were higher in the groundwater than in the ash pond discharge. The significant factor effectuating the total mass in the ash pond surface discharge as compared to the groundwater flux was flow. Flow from the ash pond during 1976 averaged 1.0 x 10^8 liters per day, whereas, the calculated total flow through the combined clay-silt and sand strata was 16,909 liters per day--only 0.016 percent of the ash pond discharge.

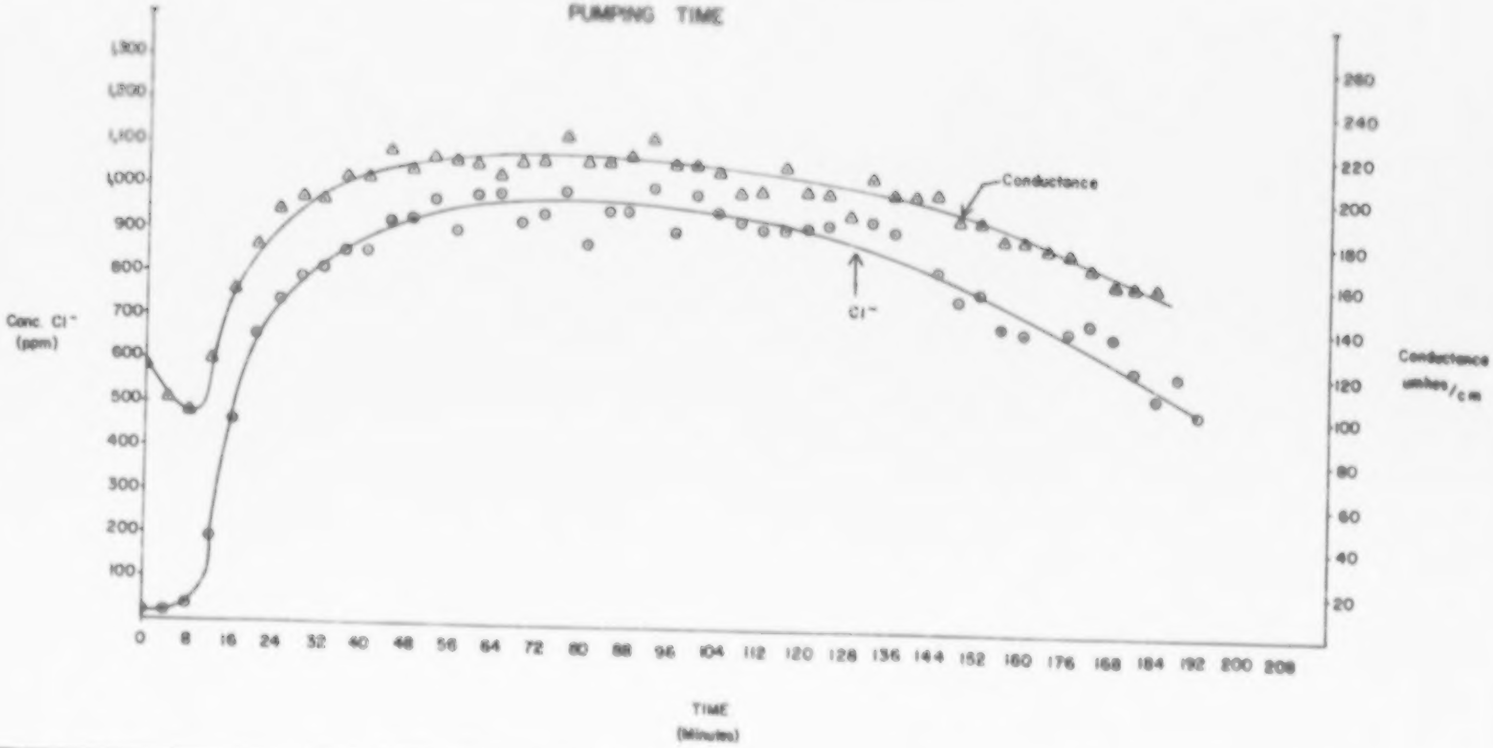
The physical measurements of the predominantly clay-silt substrata necessary to quantify groundwater flow at plant L, were not made because the large area involved would have required numerous and costly exploratory borings. The low permeabilities measured in the clay-silt substratum (less than 10^{-8} cm/sec) would, however, tend to minimize leachate movement if a generalization can be made from the calculations made with plant J's data.

As previously mentioned in the geological description (section 3), the primary material underlying the ash disposal area at plant L, is a mixture of alluvial and terrace deposits. In certain areas, such as location L4, these deposits consist of unconsolidated materials containing as much as 40 percent gravel. This type of material could not be collected in a Shelby tube for the determination of permeability. In order to determine the groundwater flow in this material, two wells were installed 1.5 meters apart with perforations transecting the pervious gravel material vertically. The difference in hydraulic head between the two wells was 3.1 meters. Nineteen liters of a saturated sodium chloride solution were then injected into the upgradient well. The downgradient well was then pumped and samples collected periodically for the measurement of conductance and chloride. Figure 17 shows a plot of chloride concentration and conductivity versus pumping time for the downgradient well. The figure indicates that the chloride concentration increased substantially within 24 minutes and reached a maximum at approximately 75 minutes. The plot of conductance versus time presents a shape nearly identical to the chloride plot, with a slight decrease in the beginning and a slower return to baseline being the only differences. The slow return to baseline of both parameters is thought to be a result of lateral dispersion of the solute.

Under the conditions of this test, if the time required to reach maximum concentration is assumed to be the flow time between the two wells, then 0.03 cm/sec would be the velocity of the ground water in this material. Using Darcy's law, this velocity converts to a permeability (K) of 0.14 cm/sec, substantially higher than values measured in the laboratory on other subsurface materials. At plant L, there are two locations (L4 and L5) where this highly permeable alluvial material was found. The water quality at both these locations, however, was not significantly different from the background wells 10CW and 11CW. This seemed to indicate that attenuation processes in the overlying clay-silt stratum were precluding ash leachate from infiltrating the porous alluvial material. However, if the ash leachate should ever enter the highly permeable alluvium, minimal attenuation, characteristic of this type of material, would allow the rapid lateral spread of ash leachate.

Figure 17

TRACER TEST OF CONDUCTANCE AND CHLORIDE
vs
PUMPING TIME



SECTION 8

LABORATORY ATTENUATION STUDIES

This section presents the results of the soil column attenuation studies performed on natural soils from plants L and J, and kaolinite clay.

ATTENUATION BY NATURAL SOIL COLLECTED AT PLANT L

A sample of the ash pond dike material from plant L was one of three soil materials used in the attenuation experiment described in section 4. As previously mentioned in that section, samples of the soil column effluent were analyzed for the constituents listed in Table 8. These data are tabulated, along with an analysis of the ash leachate used in the attenuation studies, and are presented in appendix C. The soil sample from plant L, was also analyzed by X-ray diffraction for quartz, and the clay minerals montmorillonite, kaolinite, and illite. The analysis found the clay minerals present in the following relative abundance: kaolinite > montmorillonite > illite, and quarts was the most predominate crystalline phase present.

Figures 18, 19, 20, and 21 are plots of plant L's soil column effluent concentrations for magnesium, sodium, potassium, aluminum, barium, copper, zinc, nickel, and sulfate, versus the cumulative effluent volumes. Also shown on these plots are the "initial" influent leachate concentrations for the above parameters. In Figure 18, magnesium, sodium, and potassium are plotted. The illustration shows that the concentrations of magnesium and sodium in the column effluent exceeded the initial influent concentration for the duration of the experiment, indicating solubilization of these elements occurred in the soil. Potassium, however, initially had a concentration less than the influent, which increased above the influent in subsequent samples and eventually equilibrated (concentration in equaled concentration out) with the initial leachate concentration. This seems to indicate that potassium was initially attenuated by the soil, and later merely passed through the column unaffected. This is further illustrated in Table 22, where mass balances have been calculated on twelve parameters including those illustrated in Figures 18 through 21.

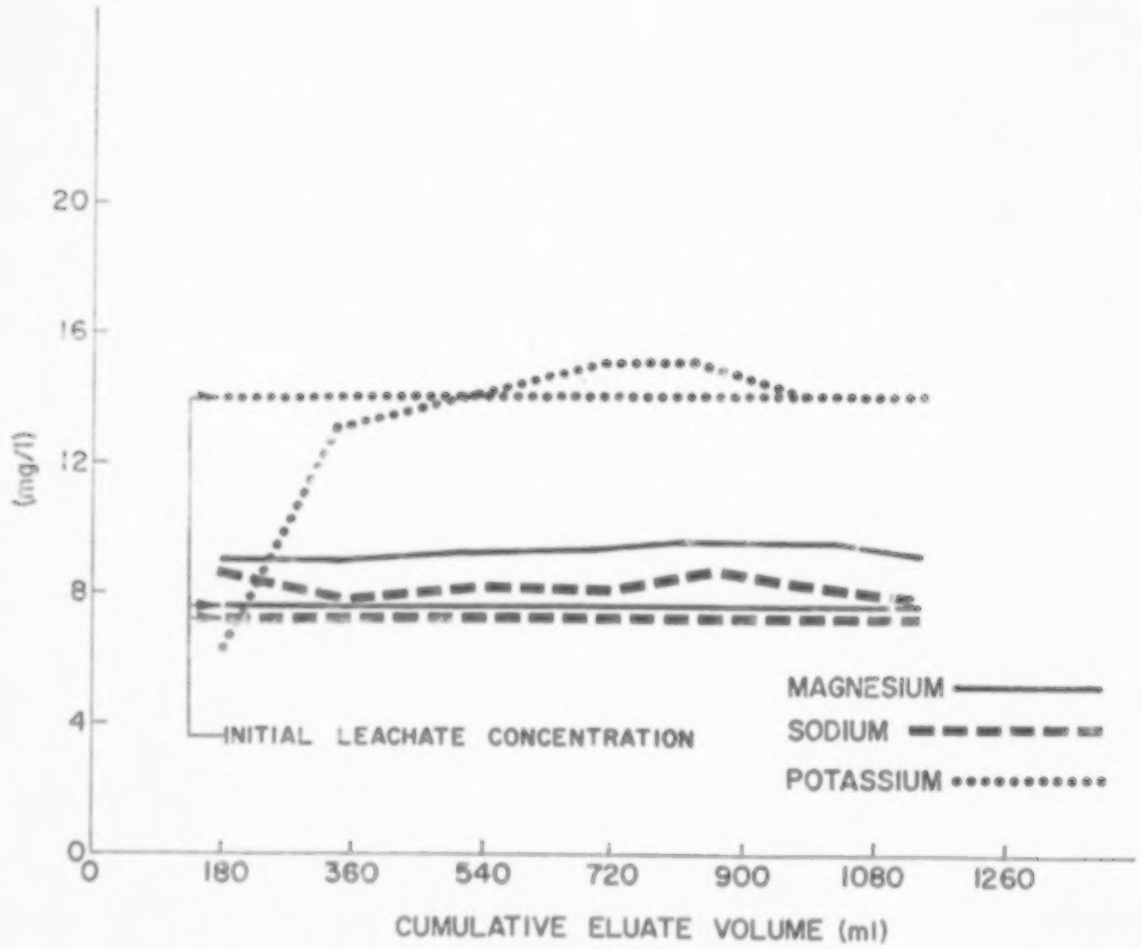


Figure 18. Concentrations of magnesium, sodium, and potassium in the effluent from plant L's soil column.

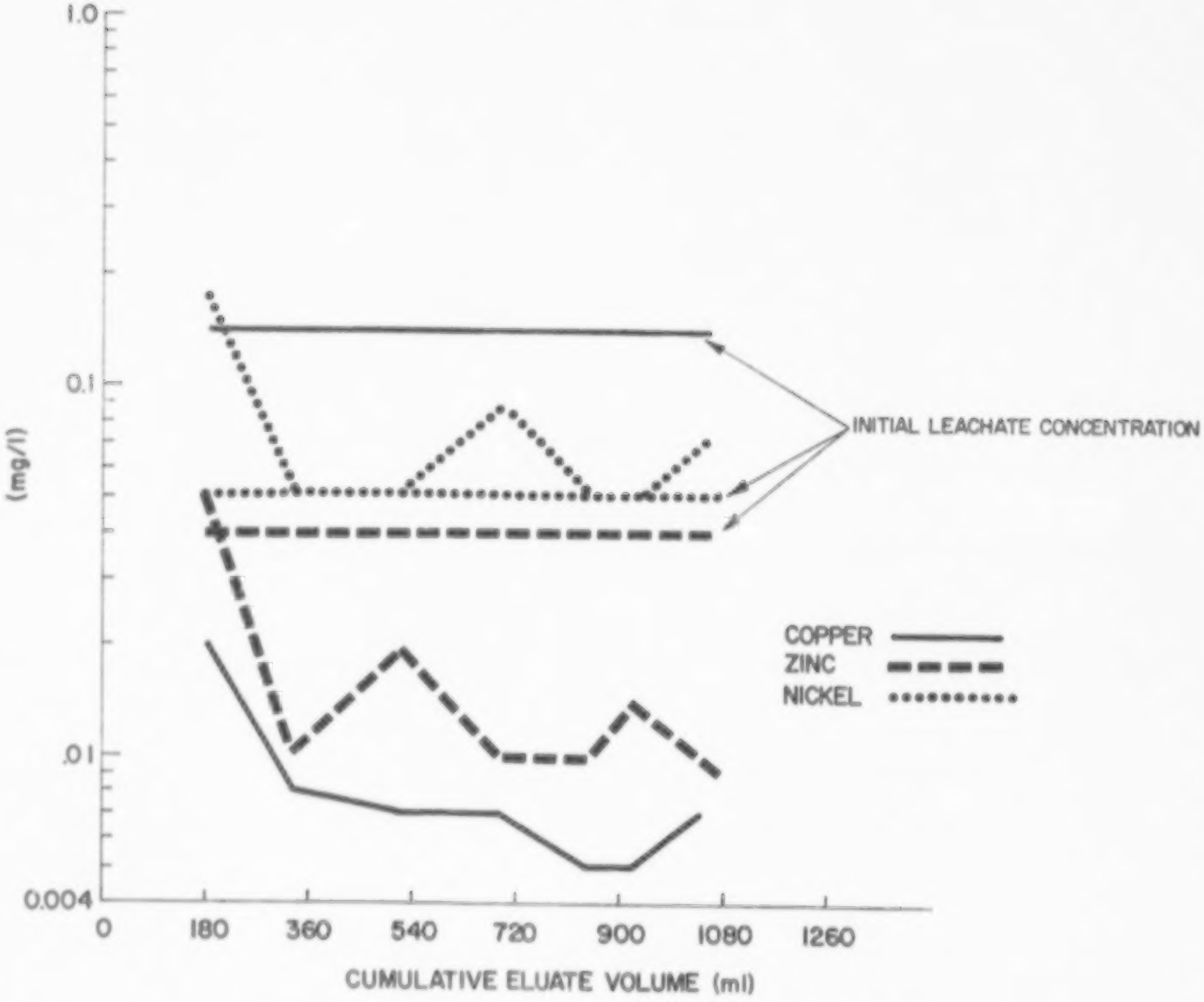


Figure 19. Concentrations of copper, zinc, and nickel in the effluent from plant L's soil column.

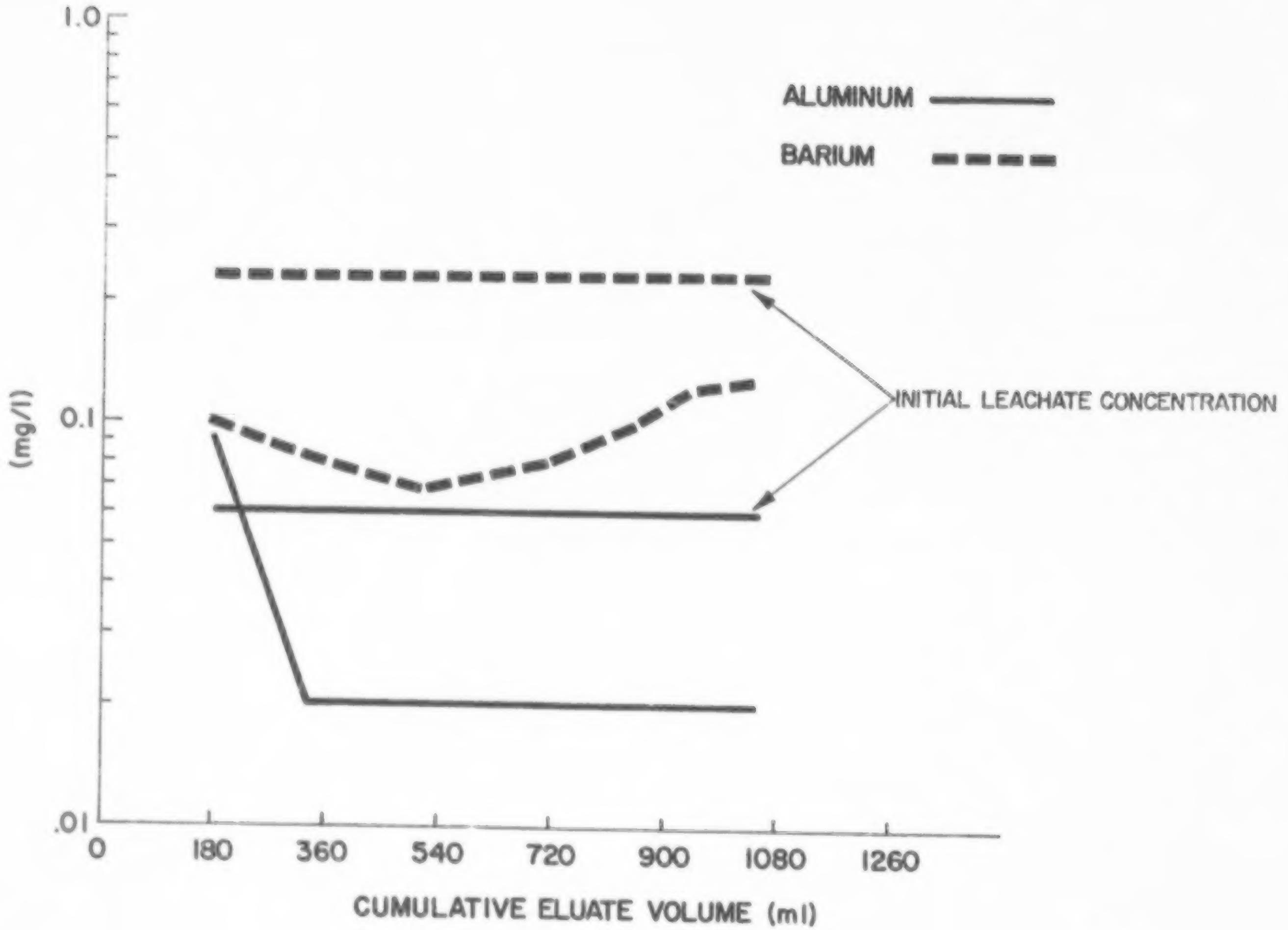


Figure 20. Concentrations of aluminum and barium in the effluent from plant L's soil column.

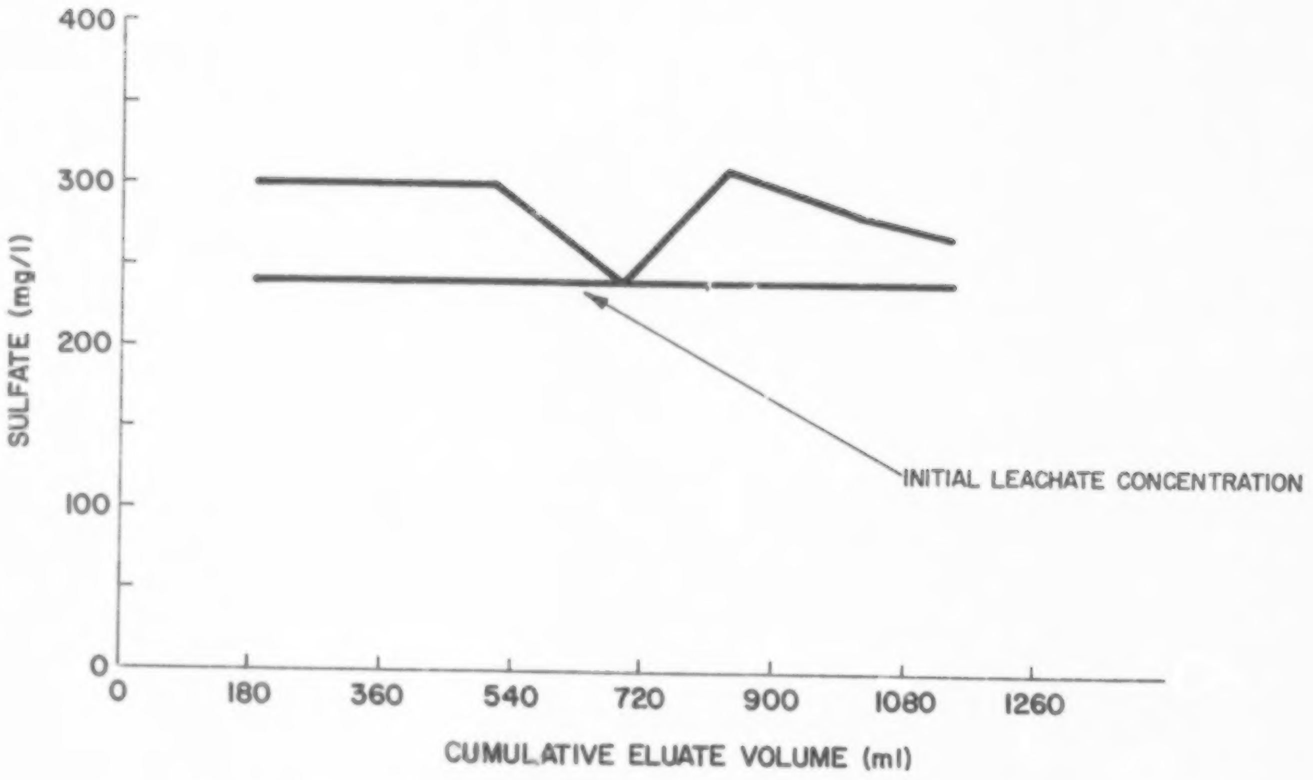


Figure 21. Concentration of sulfate in the effluent from plant L's soil column.

The mass input to the soil columns was determined by multiplying the total volume of eluate that passed through the column by the initial influent concentration. To determine the mass output of the column, the volume of each composite eluate sample was multiplied by the concentration of the constituent measured therein, and these values summed. The difference between the mass in and mass out is the amount retained, or contributed by the soil column. These data indicate that magnesium and sodium had, respectively, 16 and 5 percent increases in mass between the influent and effluent of the soil column, while 3 percent of the potassium was removed in the soil.

In Figure 19, copper, nickel, and zinc concentrations in the soil column effluent are plotted. Copper concentrations were less than the initial leachate concentration in all samples analyzed, and gradually decreased with the volume eluted. Zinc showed a trend similar to copper. With the exception of the first sample, all samples analyzed for zinc were less than the initial leachate concentration. The concentration of nickel in the leachate was less than the analytical detection limit, which accounts for effluent values not plotted below the initial leachate concentration line. However, samples of the soil column effluent did contain some measureable quantities of nickel indicating solubilization from the soil. In Table 22, the data indicate that copper and zinc had, respectively, 97 and 40 percent removal during the test. Calculations were not performed for nickel because it was not detected in the leachate.

The concentrations of aluminum and barium in the effluent from plant L's soil column are illustrated in Figure 20, and the plot for sulfate in Figure 21. All of the effluent samples analyzed for barium and aluminum had concentrations less than the initial leachate value, with the first eluate volume for aluminum being the only exception. The data in Table 22, show that 70 percent of the aluminum and 57 percent of the barium were removed in the soil column. The sulfate plot in Figure 21, indicates solubilization occurring within the soil column. This indication is supported by the mass balance data in Table 22, which shows a 15 percent increase in sulfate mass between the soil column influent and effluent.

Calcium, manganese, iron, and mercury data are not plotted, but from the mass balance data in Table 22, it is indicated that 11 percent of the calcium, 85 percent of the manganese, essentially 100 percent of the iron, and 87 percent of the mercury were removed in the soil column. Cadmium, chromium, lead, beryllium, and selenium were all less than the minimum detectable limits in all samples, including the initial leachate sample, and for that reason were not addressed in this analysis.

Also presented in Table 22, are the number of chemical equivalents removed from the leachate and the number added to the soil column effluent, with the sum of both listed at the bottom of the table. These

TABLE 22. MASS BALANCE OF PLANT L'S SOIL COLUMN INFLUENT AND EFFLUENT

Constituent	Mass IN (mg)	Mass OUT (mg)	Percent removal	Equivalents removed	Percent increased	Equivalents added
Magnesium	8.66	10.03	0	0	16	0.11
Sodium	8.44	8.87	0	0	5	0.02
Potassium	15.96	15.45	3	0.01	0	0
Copper	0.16	0.01	97	0.004	0	0
Zinc	0.05	0.03	40	0.0004	0	0
Aluminum	0.07	0.02	70	0.01	0	0
Barium	0.26	0.11	57	0.002	0	0
Sulfate	273.6	315.3	0	0	15	0.87
Calcium	210.9	187.8	11	1.16	0	0
Manganese	4.79	0.74	85	0.15	0	0
Iron	17.1	<0.01	>99	0.92	0	0
Mercury	0.0023	0.0003	87	1.9×10^{-5}	0	0
Total				2.26		1.00

data indicate that 2.26 meq (milliequivalents) were removed in the soil column, while 1.0 meq was added to the column effluent. This amounted to a net decrease of 1.26 meq through the soil column.

ATTENUATION BY NATURAL SOIL COLLECTED AT PLANT J

A sample of plant J's ash pond dike material was used to determine the attenuation of coal-ash leachate by a natural soil type being used in ash pond construction, as was the soil from plant L, previously discussed. The soil sample from plant J, contained a percentage of clay minerals that when subjected to X-ray diffraction analysis were found to be present in the following relative abundance: illite > kaolinite > montmorillonite. In addition to these clay minerals, the soil contained quartz as the most predominant crystalline phase. The cation exchange capacity of the soil was 17.0 meq per 100 grams, as determined by the method of Bascomb, which is described in appendix A.

In Figures 22 through 24, plant J's soil column effluent concentrations are plotted against the cumulative effluent volumes for magnesium, sodium, potassium, aluminum, barium, copper, zinc, and nickel. The initial leachate concentrations for the above parameters are also shown in these plots. In Figure 22, magnesium, sodium, and potassium are plotted. The illustration shows that the concentrations of magnesium and sodium in the soil column effluent exceeded the influent concentration in all samples analyzed during the experiment. Again, as with plant L's soil column study, the plots indicated solubilization of these elements within the soil column. The plot for potassium is similar to the one generated from plant L's attenuation data. Initially the effluent concentration was less than the influent, and then gradually increased to nearly the same concentration, but never quite equilibrated with the influent. This indicates that potassium was being attenuated, to some degree, for the duration of the experiment. This is also illustrated in Table 23, where mass balances have been calculated on eleven constituents, in a manner previously described. As the data in this table indicate, magnesium and sodium had, respectively, 20 and 10 percent increases in mass between the influent and effluent of the soil column, while 12 percent of the potassium was removed in the soil.

Figure 23 illustrates the plotted concentrations of copper, zinc, and nickel in plant J's soil column effluent. Copper concentrations fluctuated, but were always less than the influent value. The zinc concentration in the column effluent initially was higher than the influent, but immediately declined to remain less than the influent value for the experiment's duration. The mass balance data from Table 23 show that copper and zinc, respectively, had 94 and 57 percent removal of mass in the soil column. A balance on nickel could not be calculated because it was not detected in most samples.

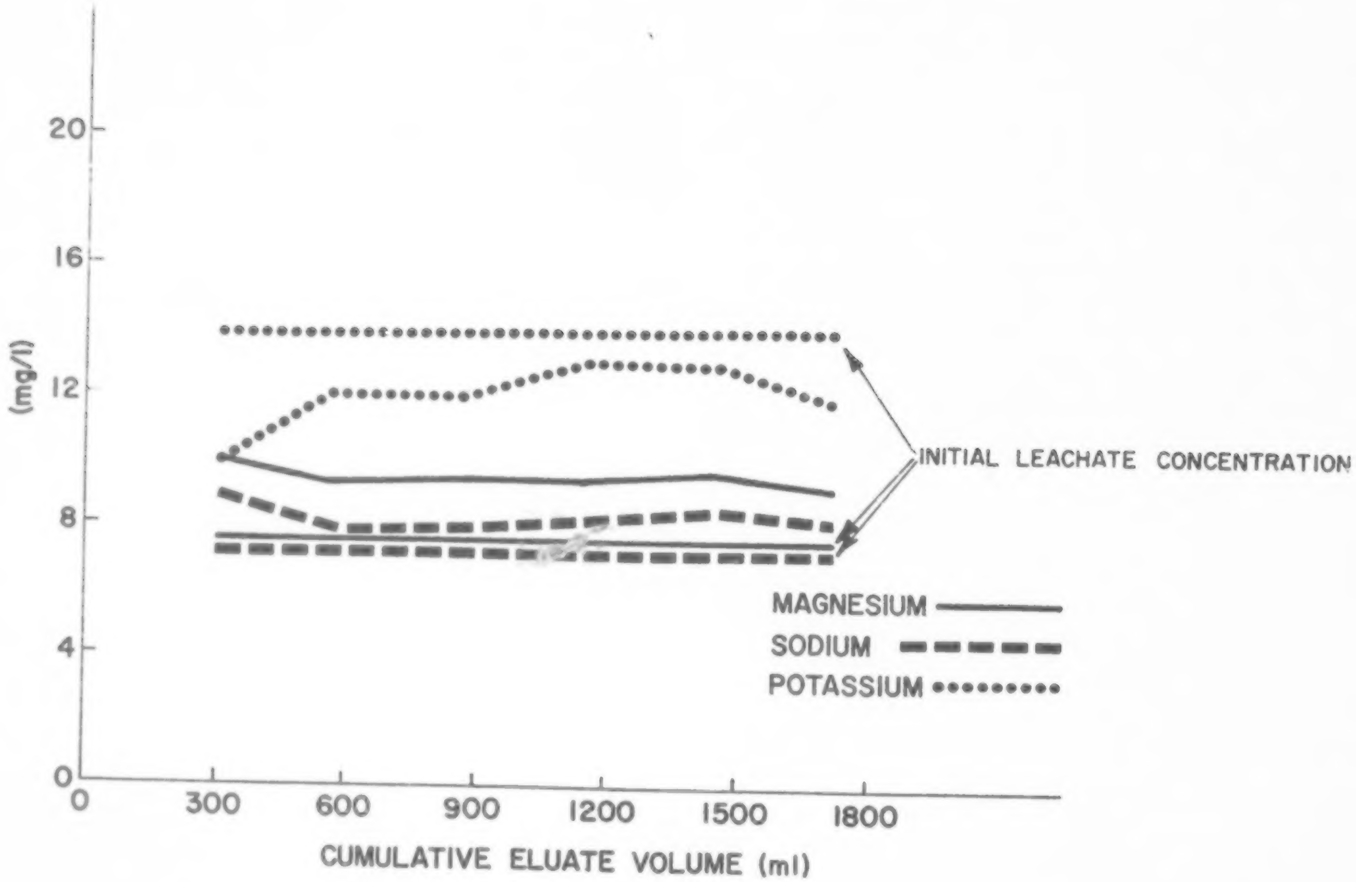


Figure 22. Concentrations of magnesium, sodium, and potassium in the effluent from plant J's soil column.

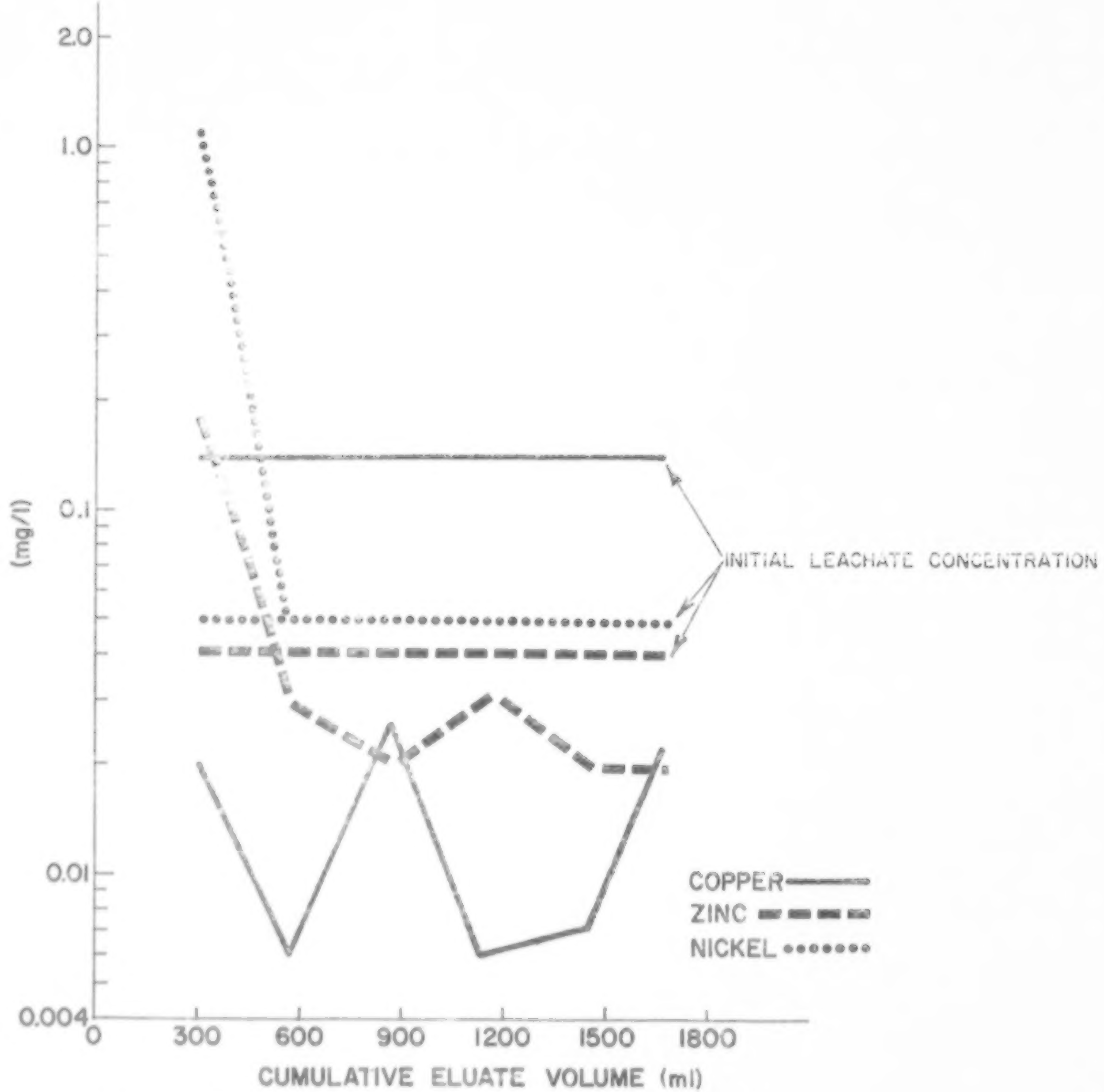


Figure 23. Concentrations of copper, zinc, and nickel in the effluent from plant J's soil column.

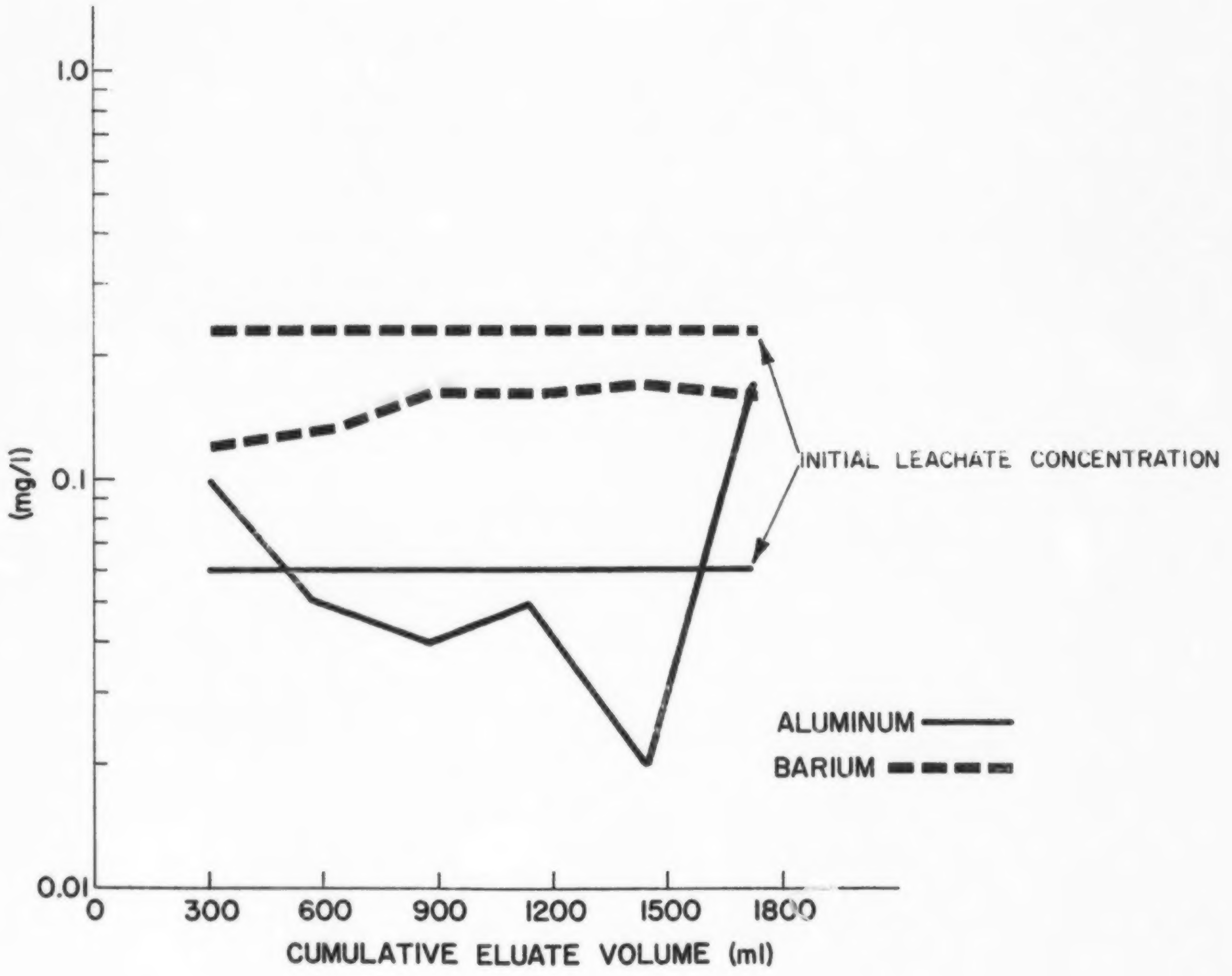


Figure 24. Concentrations of aluminum and barium in the effluent from plant J's soil column.

TABLE 23. MASS BALANCE OF PLANT J'S SOIL COLUMN INFLUENT AND EFFLUENT

Constituent	Mass IN (mg)	Mass OUT (mg)	Percent removal	Equivalents removed	Percent increased	Equivalents added
Magnesium	13.00	15.65	0	0	20	0.22
Sodium	12.31	13.59	0	0	10	0.06
Potassium	23.94	21.18	12	0.07	0	0
Copper	0.24	0.01	94	0.01	0	0
Zinc	0.07	0.04	57	0.0009	0	0
Aluminum	0.10	0.11	0	0	10	0.001
Barium	0.39	0.27	32	0.001	0	0
Calcium	316.35	261.30	17	2.75	0	0
Manganese	7.18	1.77	75	0.20	0	0
Iron	26.65	0.08	≈100	1.38	0	0
Total				4.41		0.28

Aluminum, however, began with an effluent concentration greater than the influent, then decreased to below the influent value where it remained for all samples except the last which was again greater in concentration than the influent. Barium had 32 percent removal within the soil column, according to the data in Table 23. Aluminum had a 10 percent increase in mass between influent and effluent.

Although the data for calcium, manganese, and iron were not plotted, the mass balance data in Table 23 indicate that 17 percent of the calcium, 75 percent of the manganese, and nearly 100 percent of the iron was removed in the soil column. Cadmium, chromium, lead, beryllium, mercury, and selenium were all less than their analytical detection limits in nearly all samples. Not enough sample was collected for sulfate analysis. Table 23 also shows that 4.41 chemical meq were removed in the soil column from plant J, while 0.28 meq were added to the column effluent. Thus, a net decrease of 4.13 meq occurred between the soil column influent and effluent.

ATTENUATION BY KAOLINITE

In natural soils there are three major clay minerals that may be present in relative amounts depending on the geographical location; they are kaolinite, montmorillonite, and illite. Each of these clays has the ability to attenuate pollutants from aqueous solutions, although selectively and at different rates.[25] Attempts were made to study the attenuation of coal-ash leachate by each of these clays. However, expansion of the clay minerals montmorillonite and illite upon wetting inhibited percolation to such a degree that experiments with these two clays were abandoned. It was possible, however, to study the attenuation capabilities of kaolinite. The results of that investigation are presented in Figures 25 through 27, and Table 24.

In Figure 25, column effluent concentrations of magnesium, sodium, and potassium are plotted against the cumulative eluate volume from the kaolinite clay column. The illustration shows that concentrations of magnesium and sodium in all effluent samples analyzed, except the last, exceeded the influent leachate concentration. This indicates that solubilization of these two elements occurred within the clay column. Potassium, on the other hand, had concentrations in the column effluent which exceeded the influent concentrations in all samples except the first and last. This would seem to indicate that potassium is also being solubilized to some degree within the clay column. In Table 24, mass balance data agree with the plotted data, in that magnesium, sodium, and potassium respectively, had 23, 17, and 9 percent increases in mass between the clay column influent and effluent.

Figure 26 illustrates the plotted concentrations of copper, zinc, and nickel in the kaolinite column effluent. Copper concentrations were less in the column effluent than in the influent for all samples except

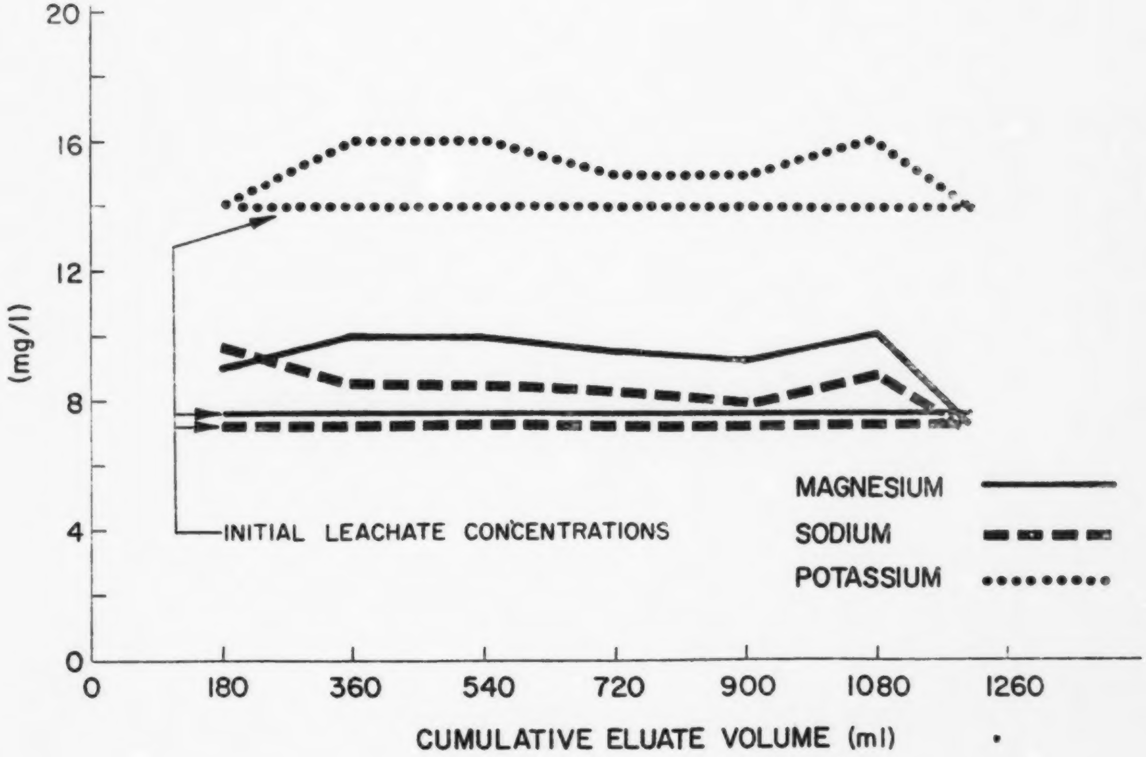


Figure 25. Concentrations of magnesium, sodium, and pottasium in the kaolinite clay column effluent.

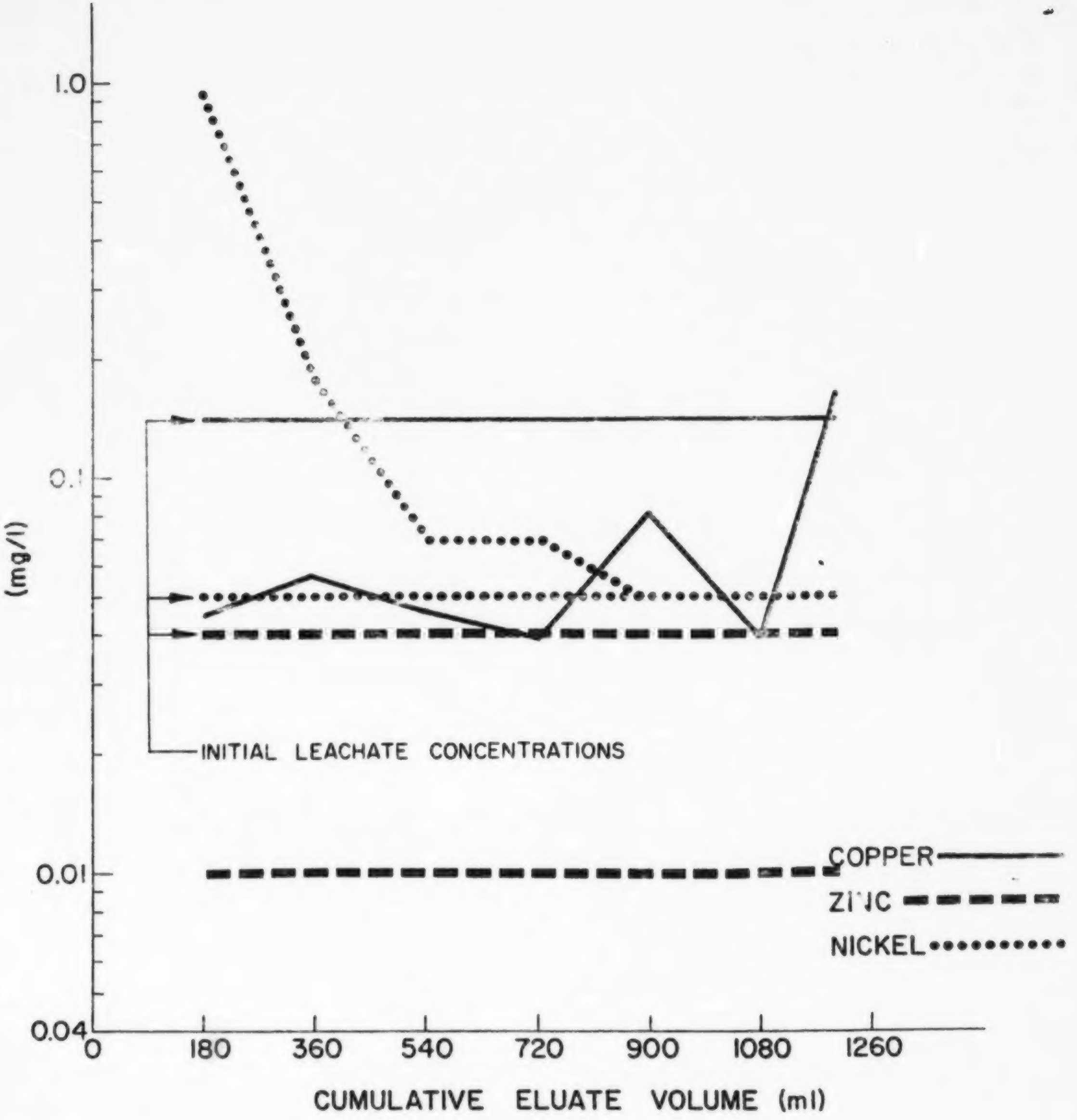


Figure 26. Concentrations of copper, zinc, and nickel in the kaolinite clay column effluent.

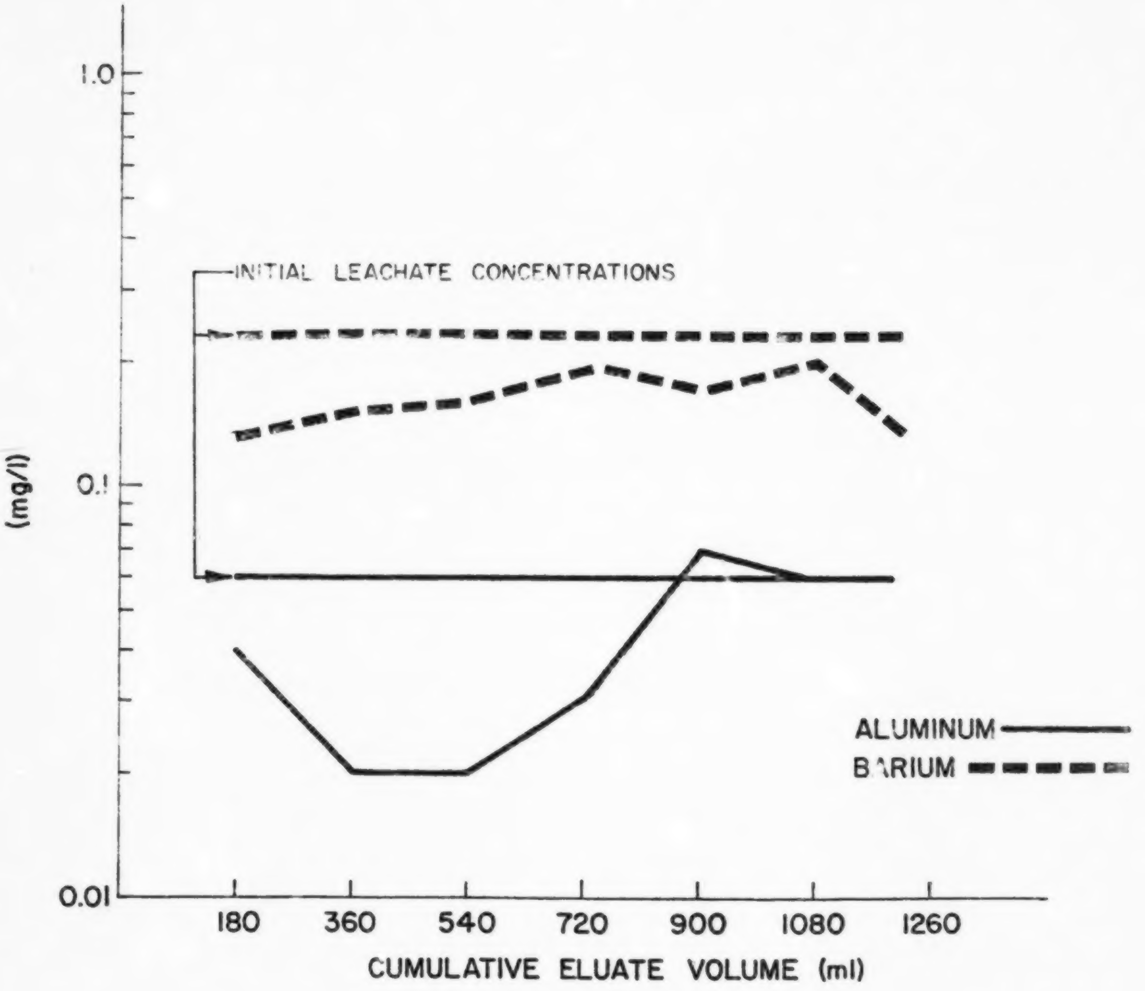


Figure 27. Concentrations of aluminum and barium in the kaolinite clay column effluent.

TABLE 24. MASS BALANCE OF KAOLINITE PACKED COLUMN INFLUENT AND EFFLUENT

Constituents	Mass IN (mg)	Mass OUT (mg)	Percent removal	Equivalents removed	Percent increased	Equivalents added
Magnesium	9.12	11.21	0	0	23	0.17
Sodium	8.64	10.11	0	0	17	0.06
Potassium	16.80	18.24	0	0	9	0.03
Copper	0.17	0.07	56	0.003	0	0
Zinc	0.05	0.03	50	0.001	0	0
Aluminum	0.07	0.05	30	0.002	0	0
Barium	0.28	0.20	29	0.001	0	0
Calcium	222.00	180.00	19	2.09	0	0
Manganese	5.04	0.99	80	0.14	0	0
Iron	18.00	0.05	99.7	0.96	0	0
Mercury	0.0024	0.0003	88	0.000021	0	0
Sulfate	345.60	429.60	0	0	24	1.75
Total				3.20		2.01

the last. All effluent zinc samples analyzed were less than the influent leachate concentration. The concentration of nickel in the column effluent initially exceeded the column influent, then decreased to equilibrate with the influent concentration, which was nickel's minimum detectable limit. Copper and zinc removal within the clay column, based on mass balance data in Table 24, was respectively 56 and 50 percent. A balance on nickel was not calculated because it was not detected in the influent and most of the effluent samples.

Plots of aluminum and barium concentration in the kaolinite column effluent are illustrated in Figure 27. All samples analyzed for barium had concentrations less than the initial leachate concentration. Aluminum concentrations were less than the influent in the early eluate volumes, then gradually increased to become equal with the influent concentration. The data from Table 24 indicates that aluminum and barium were reduced in the kaolinite column by 30 and 29 percent, respectively.

For calcium, manganese, iron, and mercury, the mass balance data in Table 24 indicate that 19 percent of the calcium, 80 percent of the manganese, nearly 100 percent of the iron, and 80 percent of the mercury was removed in the kaolinite clay column. Sulfate had a 24 percent increase in mass from influent to effluent.

In Table 24, the data also indicates that 3.20 chemical meq were removed in the kaolinite column, while 2.01 meq were added to the column effluent. As a result, a net of 1.19 chemical meq were attenuated from the initial leachate influent by the kaolinite clay column.

DISCUSSION OF LEACHATE ATTENUATION STUDY

The attenuation processes that occur in soils are a potential major influence precluding groundwater contamination by leachate from coal ash disposal areas. In an attempt to determine the extent of ash leachate attenuation by various soils, the laboratory investigations reported on above were conducted. Other investigators have used this technique to determine the attenuation of various aqueous wastes by different soils, clays, and other porous material.[26,27,28]

For example, in a study by Griffin, et al,[26] the attenuation of pollutants in municipal landfill leachate by the clay minerals montmorillonite, kaolinite, and illite was investigated. Their study determined the following clay mineral hierarchy for attenuation capabilities, montmorillonite > illite > kaolinite, and that the principal attenuation mechanism for lead, cadmium, mercury, and zinc was precipitation in the soil columns surface layers. In a study by Fetter[27] to determine attenuation of secondarily treated wastewater by a calcareous glacial outwash soil, the findings suggested that heavy metals removal was through ion exchange. Still other investigators, such as Leeper,[28] consider the adsorption reactions with hydrous oxides of iron, aluminum, and manganese to be the major mechanism for the attenuation of metals in soil. As one can see from this small, but representative sampling, the literature is inconclusive as to which mechanism is the major factor influencing attenuation by soils. Indeed, no one mechanism is universally responsible for the attenuation processes that occur in soils receiving liquid wastes or leachate. In fact, the mechanisms may vary for each situation depending on the characteristics of the soil, the characteristics of the liquid waste or leachate, and the hydrological conditions.

The major mechanism influencing attenuation of ash leachate in this study is not readily discernable from the previously discussed data. It may be concluded with a certain degree of confidence, however, that ion exchange is not solely responsible for the removal of constituents from the ash leachate, for the following reason.

The two natural soils from plants L and J, and the kaolinite clay used in the column tests had cation exchange capacities, respectively, of 20.0, 17.0, and 16.0 meq per 100 g (the cation exchange capacity of the silica was negligible at 1.2 meq/100 g). Five grams each of the soils and clay material was used in each column, which yielded a total exchange capacity for the columns of 1.0 meq plant L material, 0.85 meq plant J material, and 0.80 meq for the kaolinite column. The number of meq's attenuated by these same respective columns was 1.26, 4.13, and 1.19 meq. Each column has thus exceeded its available exchange capacity; consequently, ion exchange is not the only mechanism accounting for attenuation in this study. Actually, ion exchange may be only a minor influence, and precipitation and/or adsorption may be the major influencing mechanisms affecting attenuation, but the data do not differentiate between these two mechanisms.

A comparison of the mass balance data in Tables 22, 23, and 24 shows that magnesium and sodium had a net increase in mass between the column influent and effluent for all three attenuation experiments. This indicates that these two elements were solubilized by the ash leachate as it passed through the soil columns. Of the three materials used in this study, the kaolinite clay released the most magnesium and sodium. Potassium was also released from the kaolinite, while the two natural soils, from plants J and L, attenuated potassium.

Copper and zinc were both retained in all three attenuation columns, copper more so than zinc. Copper was attenuated the least by the kaolinite clay. The two natural soils attenuated greater than 90 percent of the copper. Barium was attenuated in all three columns, but the kaolinite clay retained the least. Aluminum was attenuated in the kaolinite column and by the soil from plant L. Aluminum solubilized in plant J's column. Calcium, manganese, and iron were all attenuated in the three columns. Iron had the largest attenuation of the constituents analyzed with essentially 100 percent removal in each column; manganese followed with 75 percent plus attenuation.

In general, soils that are composed of high percentages of clay minerals will, by one mechanism or another, tend to attenuate solutes more so than will materials containing high percentages of sand.

SECTION 9

THEORETICAL CONSIDERATIONS

Using information reported in the literature to date regarding coal-ash leachate and the attenuation of leachates in general, the results of this study, and some fundamental knowledge of the hydrogeochemical environment, a schematic diagram of ash pond leachate generation and attenuation was prepared (see Figure 28). This diagram illustrates some of the basic concepts associated with solid waste disposal in general and presents some details relating to coal-ash disposal in particular. The diagram does not necessarily indicate conditions and mechanisms associated with all ash disposal sites, but is designed to relate some of the physical and chemical processes that may be pertinent to an environmental evaluation of groundwater degradation at coal-ash disposal areas.

In this illustration, fly ash, bottom ash, and pyrites are sluiced to the ash pond, along with other miscellaneous plant discharges, such as acidic coal-pile drainage. Once in the disposal pond, the ash and other heavy particles settle out, with the supernatant overflowing into an adjacent surface water. Supernatant that does not leave the pond via the surface overflow infiltrates into the settled ash, carrying with it any solutes picked up during sluicing of the ash from the plant and mixing with other wastes discharged to the pond. After infiltration, the pond supernatant percolates down through the saturated aerobic zone where readily soluble ions of calcium, magnesium, sodium, and sulfate are added to solution. Some slight dissolution of certain metals may occur, and sulfite, if not already in solution, solubilizes.

Further downward percolation leads to the anoxic zone, which is created by the depletion of dissolved oxygen by sulfite or other oxidation processes. It is in the anoxic zone, which occurs either below the water table or deep enough to prevent surface aeration, where the percolating water acquires the culmination characteristics of coal-ash leachate. The anoxic zone is a reducing acidic environment in which dissolution of metals can occur, sulfides are formed, and high concentrations of ferrous iron may occur. It is also in this zone where the hydraulic gradient of the groundwater begins to exert its energy potential on the leachate, altering the direction component of its velocity from strictly downward to lateral.

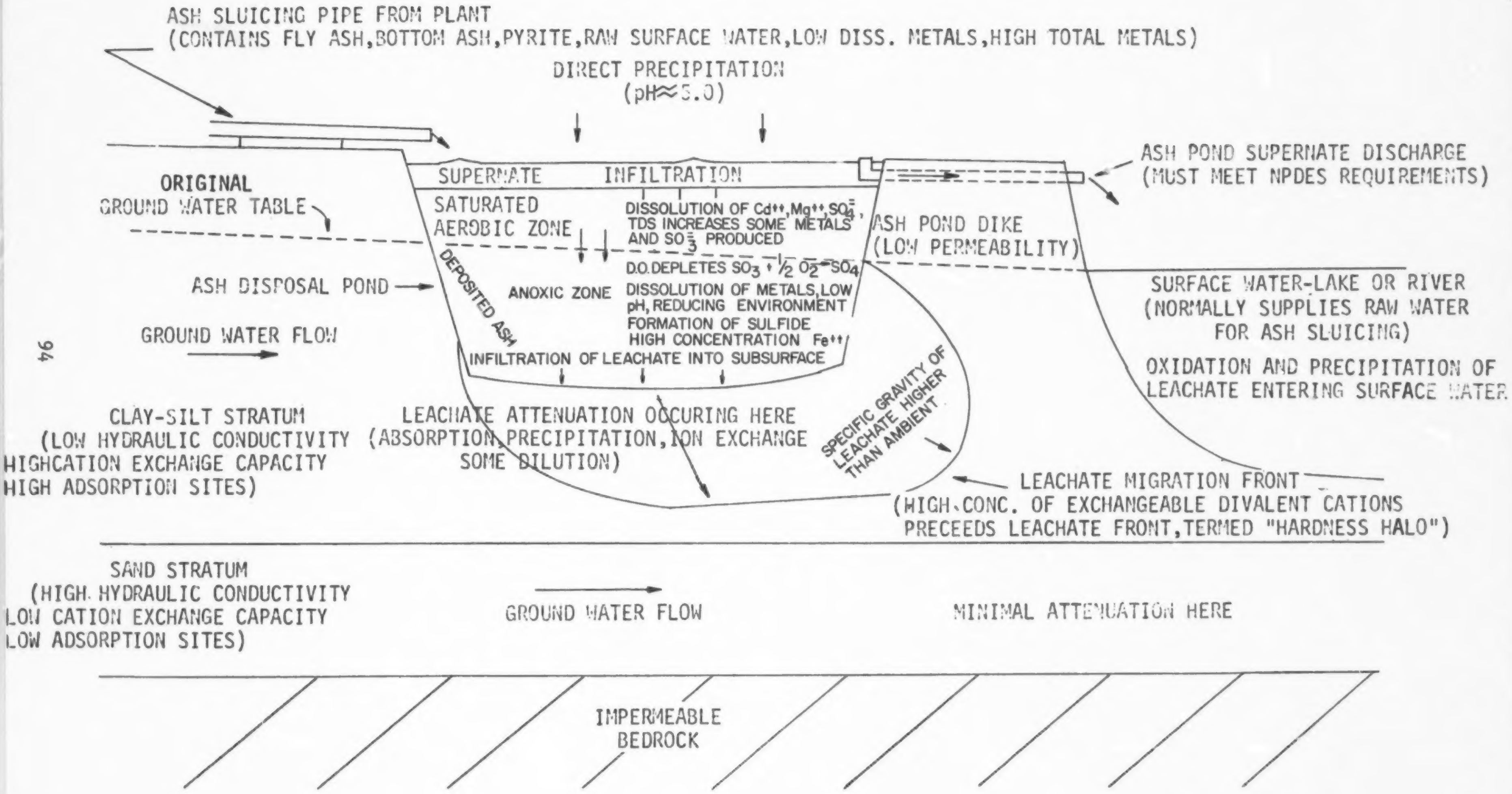

ASH SLUICING PIPE FROM PLANT
(CONTAINS FLY ASH,BOTTOM ASH,PYRITE,RAW SURFACE WATER,LOW DISS. METALS,HIGH TOTAL METALS)
DIRECT PRECIPITATION
($pH \approx 5.0$)
ASH POND SUPERNATE DISCHARGE
(MUST MEET NPDES REQUIREMENTS)
ORIGINAL
GROUND WATER TABLE
SUPERNATE
INFILTRATION
SATURATED
AEROBIC ZONE
DISSOLUTION OF Cd^{++}, Mg^{++}, $SO_4^{=}$, TDS INCREASES SOME METALS AND $SO_3^{=}$ PRODUCED
ASH POND DIKE
(LOW PERMEABILITY)
DEPOSITED ASH
ASH DISPOSAL POND
ANOXIC ZONE
D.O. DEPLETES $SO_3 + 1/2\,O_2 \rightarrow SO_4$
DISSOLUTION OF METALS, LOW pH, REDUCING ENVIRONMENT
FORMATION OF SULFIDE
HIGH CONCENTRATION Fe^{++}
INFILTRATION OF LEACHATE INTO SUBSURFACE
SURFACE WATER-LAKE OR RIVER
(NORMALLY SUPPLIES RAW WATER
FOR ASH SLUICING)
OXIDATION AND PRECIPITATION OF
LEACHATE ENTERING SURFACE WATER
GROUND WATER FLOW
CLAY-SILT STRATUM
(LOW HYDRAULIC CONDUCTIVITY
HIGHCATION EXCHANGE CAPACITY
HIGH ADSORPTION SITES)
LEACHATE ATTENUATION OCCURING HERE
(ABSORPTION, PRECIPITATION, ION EXCHANGE
SOME DILUTION)
SPECIFIC GRAVITY OF LEACHATE HIGHER THAN AMBIENT
LEACHATE MIGRATION FRONT
(HIGH CONC. OF EXCHANGEABLE DIVALENT CATIONS
PRECEEDS LEACHATE FRONT,TERMED "HARDNESS HALO")
SAND STRATUM
(HIGH HYDRAULIC CONDUCTIVITY
LOW CATION EXCHANGE CAPACITY
LOW ADSORPTION SITES)
GROUND WATER FLOW
MINIMAL ATTENUATION HERE
IMPERMEABLE
BEDROCK

FIGURE 28. SCHEMATIC OF COAL-ASH
LEACHATE GENERATION AND ATTENUATION

Eventually the leachate begins to infiltrate the bottom of the ash disposal area. This may occur at a relatively high rate if the pond bottom is of a highly permeable material, such as sand, or at a lower rate if the material is a low permeable clay-silt, such as illustrated in Figure 28. In the clay-silt stratum attenuation of solutes in the leachate will begin to occur. Attenuation mechanisms, such as ion exchange, chemical precipitation, and physical adsorption, will act to lessen the leachate migration. As the leachate plume advances through the subsurface environment, metal ions with an affinity for adsorption and exchange sites will replace weakly-bound divalent cations, such as calcium and magnesium. These displaced divalent cations will move along preceding the leachate plume and create what has been termed a "hardness halo." Conservative constituents, such as chloride and sulfate, may even precede this hardness halo. The rate of leachate migration will depend on the hydraulic conductivity and the rate of attenuation.

If the leachate plume should reach a highly permeable stratum such as the sand stratum depicted in Figure 28, then the potential for increased groundwater degradation can occur. A sand stratum or aquifer offers little in the way of attenuation capacity and much as an avenue for leachate migration. Hydraulic conductivities of sandy material are normally greater than those of clay, and the number of adsorption and exchange sites are fewer, which will tend to decrease the rate of attenuation.

Leachate studies thus far suggest that coal-ash disposal sites, and perhaps solid waste disposal sites in general, might be constructed in such a manner as to allow leachate to percolate downward through an attenuation blanket. The attenuation blanket would need to be of design and material that would allow optimum flow and attenuation, thus acting as a treatment system.

REFERENCES

1. Merz, R. C., and J. R. Snead. "Investigation of Leaching of Ash Dumps." State Water Pollution Control Board, Sacramento, California, 1952.

2. Rohrman, F. A. "Analyzing the Effect of Fly Ash on Water Pollution." Power, 115, August 1971. pp. 76-77.

3. O'Connor, J. T., M. H. Virshbo, C. J. Cain, and C. J. O'Brien. "The Composition of Leachates from Combustion By-Products." Paper presented at the ASCE National Environmental Engineering Division Conference Symposium on Wastewater Effluent Limits, University of Michigan, Ann Arbor, Michigan, July 18-20, 1973.

4. Weeter, D. W., J. E. Niece, and A. M. DiGioia, Jr. "Environmental Management of Residues from Fossil-Fuel Power Stations." Paper presentfed at the 1974 Annual Water Poll. Control Fed. Conf., Denver, Colorado, October 8, 1974.

5. Theis, T. L., and J. L. Wirth. "Sorptive Behavior of Trace Metals on Fly Ash in Aqueous Systems." Environmental Sci. and Technol., 11(12), November 1977. pp. 1096-1100.

6. Theis, T. L. "The Potential Trace Metal Contamination of Water Resources Through the Disposal of Fly Ash." Paper presented at the 2d National Conference on Complete Water Reuse, Chicago, Illinois, May 4-8, 1975.

7. O'Brien, D. J., and F. B. Birkner. "Kinetics of Oxygenation of Reduced Sulfur Species in Aqueous Solution." Environmental Sci. and Technol., 11(12), November 1977. pp. 1114-1120.

8. Chu, T.-Y. J., W. R. Nicholas, and R. J. Ruane. "Complete Reuse of Ash Pond Effluents in Fossil-Fueled Power Plants." Paper presented at the 68th Annual Meeting of the AIChE Symposium on Water Reuse in the Chemical Industry, Los Angeles, California, November 17, 1975.

9. Reed, G. D., D. T. Mitchell, and D. G. Parker. "Water Quality Effects of Aqueous Fly Ash Disposal." Paper presented at the 31st Annual Purdue Ind. Waste Conf., Purdue University, West LaFayette, Indiana, May 4-6, 1976.

10. Burnett, J. Master's Thesis, Civil Engineering Department, University of Arkansas, Fayetteville, Arkansas, 1976.

11. Brown, J., N. J. Ray, and M. Ball. "The Disposal of Pulverized Fuel Ash in Water Supply Catchment Areas." Water Research, 10, 1976. pp. 1115-1121.

12. Harriger, T. L., W. M. Barnard, D. R. Corbin, and D. A. Watroba. "Impact of a Coal Ash Landfill on Water Quality in Northcentral Chautauqua County, New York." Departments of Geology and Chemistry, State University College, Fredonia, New York, 1977.

13. Benziger, C. P., and J. M. Kellberg. "Preliminary Geological Investigation for Eastern Area Steam Plant." TVA Division of Water Control Planning, Knoxville, Tennessee, February 1951.

14. Kellberg, J. M., and C. P. Benziger. "Geology of the Widows Creek Steam Plant Site." TVA Division of Water Control Planning, Knoxville, Tennessee, April 1950.

15. Davison, R. L., D. F. S. Natusch, and J. R. Wallace. "Trace Elements in Fly Ash Dependence of Concentration on Particle Size." Environmental Sci. and Technol., 8(13), December 1974. pp. 1107-1113.

16. Quality Criteria for Water. U.S. Environmental Protection Agency, EPA-440/9-76-023, Washington, D.C., 1976.

17. Hem, J. D. "Graphical Methods for Studies of Aqueous Aluminum Hydroxide, Fluoride, and Sulfate Complexes," Chemistry of Aluminum in Natural Water. Geological Survey Water-Supply Paper 1827-B, 1968.

18. Roberson, C. E., and J. D. Hem. "Solubility of Aluminum in the Presence of Hydroxide, Fluoride, and Sulfate." Chemistry of Aluminum in Natural Water. Geological Survey Water-Supply Paper 1827-C, 1969.

19. Hem, J. D., and W. H. Cropper. "Survey of Ferrous-Ferric Chemical Equilibria and Redox Potentials." Chemistry of Iron in Natural Water. Geological Survey Water-Supply Paper 1459, 1962.

20. Hem, J.D. "Equilibrium Chemistry of Iron in Groundwater." Principles and Applications of Water Chemistry, S.D. Frost and J.V. Hunter, eds. John Wiley, pub., 1967. (Proceedings from 4th Rudolph Research Conference, 1965.)

21. Hem, J.D. "Some Chemical Relationships Among Sulfur Species and Dissolved Ferrous Iron." Chemistry of Iron in Natural Water, Geological Survey Water-Supply Paper 1459, 1962.

22. Garrels, R.M. Mineral Equilibria. Harper and Brothers, publishers, New York, 1960

23. Cox, D. B., T.-Y. J. Chu, and R. J. Ruane. "Characterization of Coal Pile Drainage." Paper prepared for Office of Energy, Minerals, and Industry, Office of Research and Development, U.S. Environmental Protection Agency, Washington, D.C., 1978.

24. Federal Water Quality Administration. Oxygenation of Ferrous Irons. U.S. Government Printing Office, Washington, D.C., 1970.

25. Hem, J. D., "Chemistry and Occurrence of Cadmium and Zinc in Surface Water and Groundwater." Water Resources Research, 8(3), June 1972. pp. 661-679.

26. 1976 Annual Book of ASTM Standards, Part 19, Soil and Rock; Building Stones; Peats. American Society for Testing and Materials, Philadelphia, Pennsylvania, 1976.

27. Griffin, R. A., N. F. Shimp, J. D. Steele, R. R. Ruch, W. A. White, and G. Hughes. "Attenuation of Pollutants in Municipal Landfill Leachate by Passage Through Clay." Environmental Sci. and Technol., 10(13), December 1976.

28. Ibid.

29. Fetter, C. W. "Attenuation of Waste Water Elutriated Through Glacial Outwash." Ground Water, 15(5), September-October 1977.

30. Leeper, G. W. "Reactions of Heavy Metals with Soil with Special Regard To Their Application in Sewage Waste." Department Army Corps of Engineers Rep. Cont. No. DACW 73-73-C-0026, 1970.

31. Standard Methods for the Examination of Water and Wastewater. 14th ed., 1975.

32. Methods for Chemical Analysis of Water and Wastes. Environmental Monitoring and Support Laboratory, EPA-625-16-74-003a, 1976.

APPENDIX A

ANALYTICAL METHODS

APPENDIX A

ANALYTICAL METHODS

The elements, aluminum, barium, beryllium, calcium, cadmium, chromium, copper, iron, magnesium, manganese, nickel, and lead in the interstitial water, soil column effluents and groundwater well samples, were measured by direct atomic absorption spectrophotometry using techniques described in Standard Methods[29] and by EPA.[30] Mercury was determined by the cold vapor technique recommended by EPA. Arsenic and selenium were measured using the gaseous hydride method, also recommended by EPA.

Sulfate was measured using the turbidimetric method, and pH values were obtained in the field using the glass electrode. Conductivity and alkalinity were also measured in the field using established procedures.[29,30]

Soil core samples were analyzed for aluminum, barium, beryllium, calcium, cadmium, chromium, copper, iron, magnesium, manganese, nickel, and lead by first undergoing a wet acid digestion followed by direct measurement with atomic adsorption spectrophotometry.[30] Mercury was measured in the soil core samples using EPA's recommended methods.[30] Arsenic and selenium were set digested and then determined by the gaseous hydride method previously mentioned.

Standard powder X-ray diffraction techniques were used to determine the relative amounts of quartz, kaolinite, montmorillinite, and illite present in the soils.

Oxidation-reduction potentials were determined with a silver-silver chloride electrode.

Vertical and horizontal permeabilities of soil samples were determined by encasing soil specimens 3.5 cm in diameter and approximately 7.6 cm long in a rubber membrane and placing in a triaxial chamber. Back pressure to 70,310 kgs/m^2 (100 psi) was applied to assure specimen saturation. The average coefficient of permeability was then determined under a constant head test method by measuring the quantity of water flowing through the specimen in a given time.

The moisture content of soil samples was determined as per ASTM procedure D-2216. Bulk densities were determined by weighing a soil specimen 15 cm long and 8.9 cm in diameter, then coating the specimen with paraffin and submerging in water to determine its volume. The moisture content of the specimen was then determined and the bulk density calculated using the specimen's weight, volume, and moisture content.

Grain size classifications were determined by sieve separation of large particles followed by the hydrometer technique for the silt and clay fraction.

Dissolved oxygen concentrations in groundwater samples were determined in situ by lowering a membrane electrode into the monitoring wells. The membrane electrode was also used on groundwater samples brought to the surface for dissolved oxygen determinations.

DETERMINATION OF CATION EXCHANGE CAPACITY[*]

Reagents

Triethanolamine solution: Triethanolamine (commercial) 90 ml diluted to 1:1, and pH adjusted to 8.1 by adding 2N-hydrochloric acid (140-150 ml). This solution is diluted to 2:1. Protect from carbon dioxide during storage.

Barium chloride solution: $BaCl_2$, $2H_2O$ 244 g per 1 (approximately 2N).

Buffered barium chloride reagent: Mix equal volumes of the above solutions.

Magnesium sulphate solution: $MgSO_4$, $7H_2O$ 6.2 g per 1 (approximately 0.05N).

EDTA solution: Sequestric acid disodium salt 3.723 g per 1 (0.02N).

Catechol Violet indicator: 0.1 g dissolved in 100 ml of water.

Method

Transfer 5 g of soil (<2 mm air-dry, of known moisture content) to a tightly stoppered polythene centrifuge bottle. Note the weight of bottle plus soil (W_1). Treat calcareous soils with approximately 100 ml of the buffered barium chloride reagent, preferably with gentle shaking for 1 hr. Centrifuge at 1500 rpm (RCF) 415) for 15 min. and discard the supernatant liquid. For noncalcarous soils this first washing can be omitted. Treat with a further 200 ml of reagent overnight, centrifuge and again discard the supernatant liquid. Add approximately 200 ml of distilled water and shake for a few minutes to break up the soil cake. Centrifuge and discard the supernatant liquid. Weigh the bottle with contents (W_1). Pipette into the bottle 100 ml of magnesium sulphate solution and shake the stoppered bottle occasionally over a period of 2 hr. Centrifuge and transfer the clear liquid immediately to a stoppered flask.

To a 5-ml aliquot of the solution add 6 drops of 2N-aq. ammonia and titrate with standard EDTA solution using 2 drops of Catechol Violet indicator. The end-point is indicated by a color change from clear blue to reddish purple (Titre A_1 ml). This titre must be corrected for the effect of the volume (not chloride content) of liquid retained by the centrifuged soil after the wash water:

Corrected titre $(A_2) = A_1(100 + W_2\ W_1)/100$ ml

Aliquots of 5 ml of the original magnesium sulphate solution are also titrated under similar conditions (Titre B).

CEC of the soil = $8(B - A_2)$ meq/100 g

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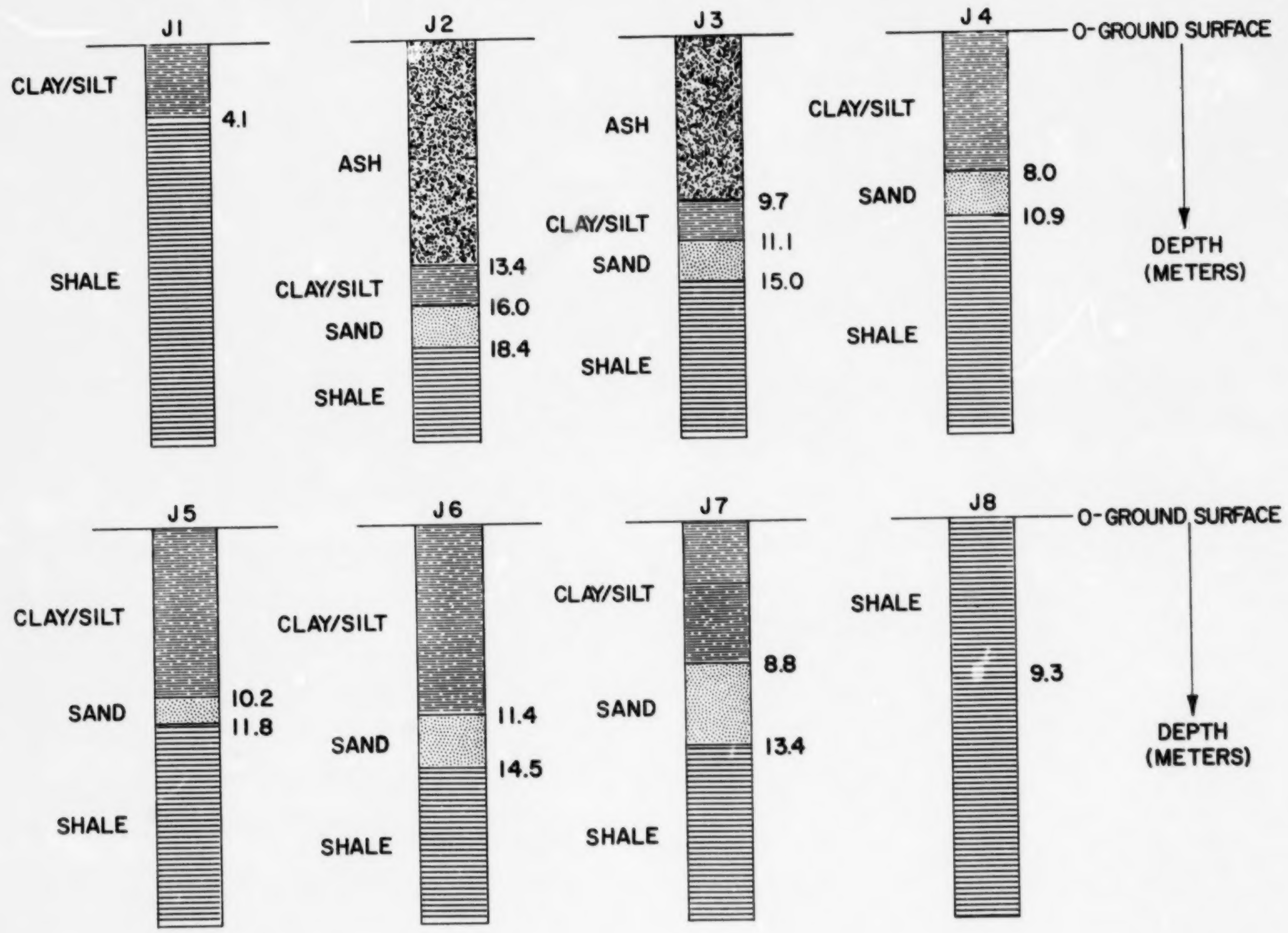
[*] Bascomb, C. L. "Rapid Method for the Determination of Cation-Exchange Capacity of Calcareous and Noncalcareous soils." J. of Sci. Food and Agric., 15, 1964. pp. 821-823.

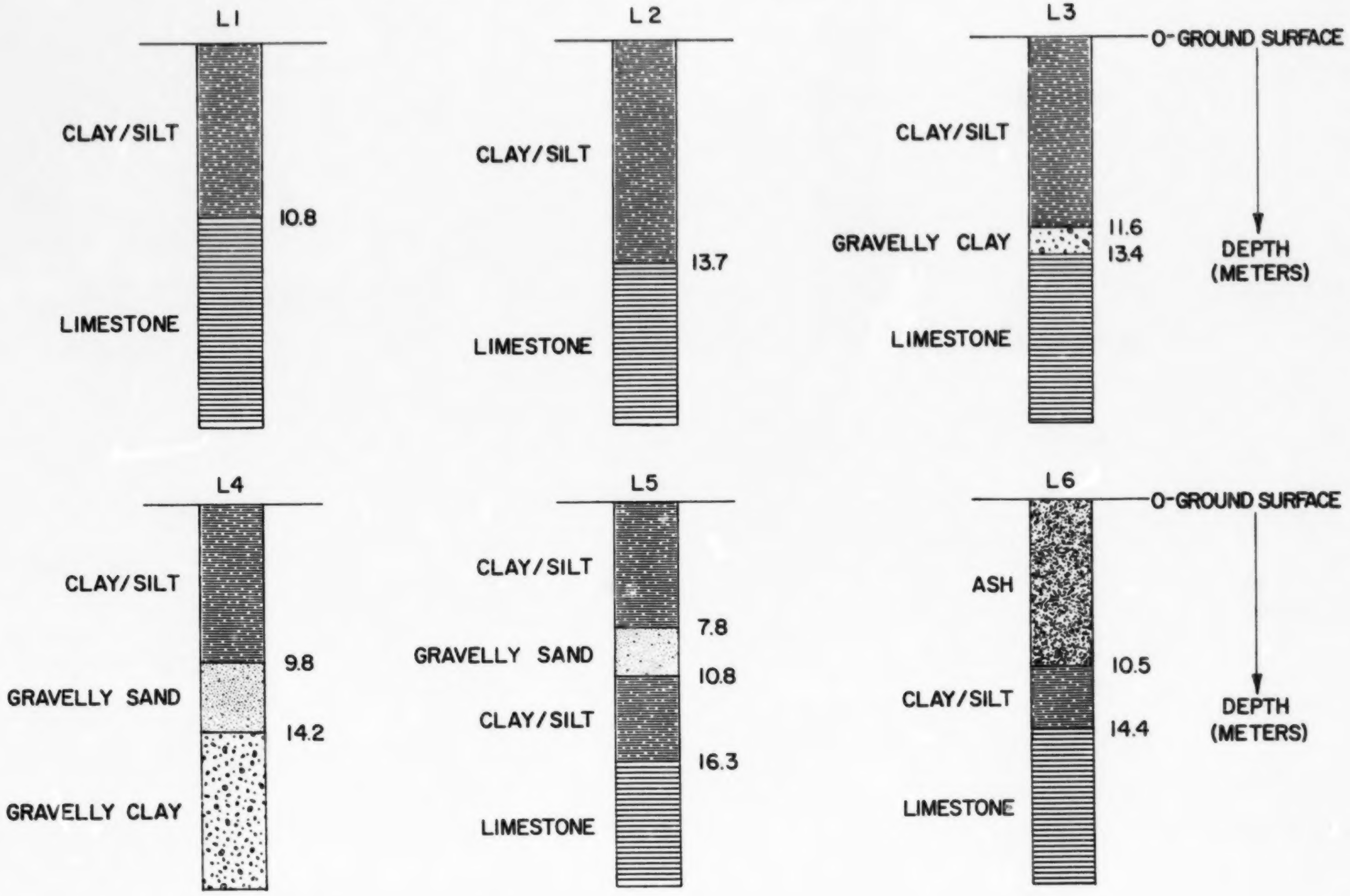
APPENDIX B

VERTICAL PROFILES OF SUBSTRATUM AT PLANTS J AND L

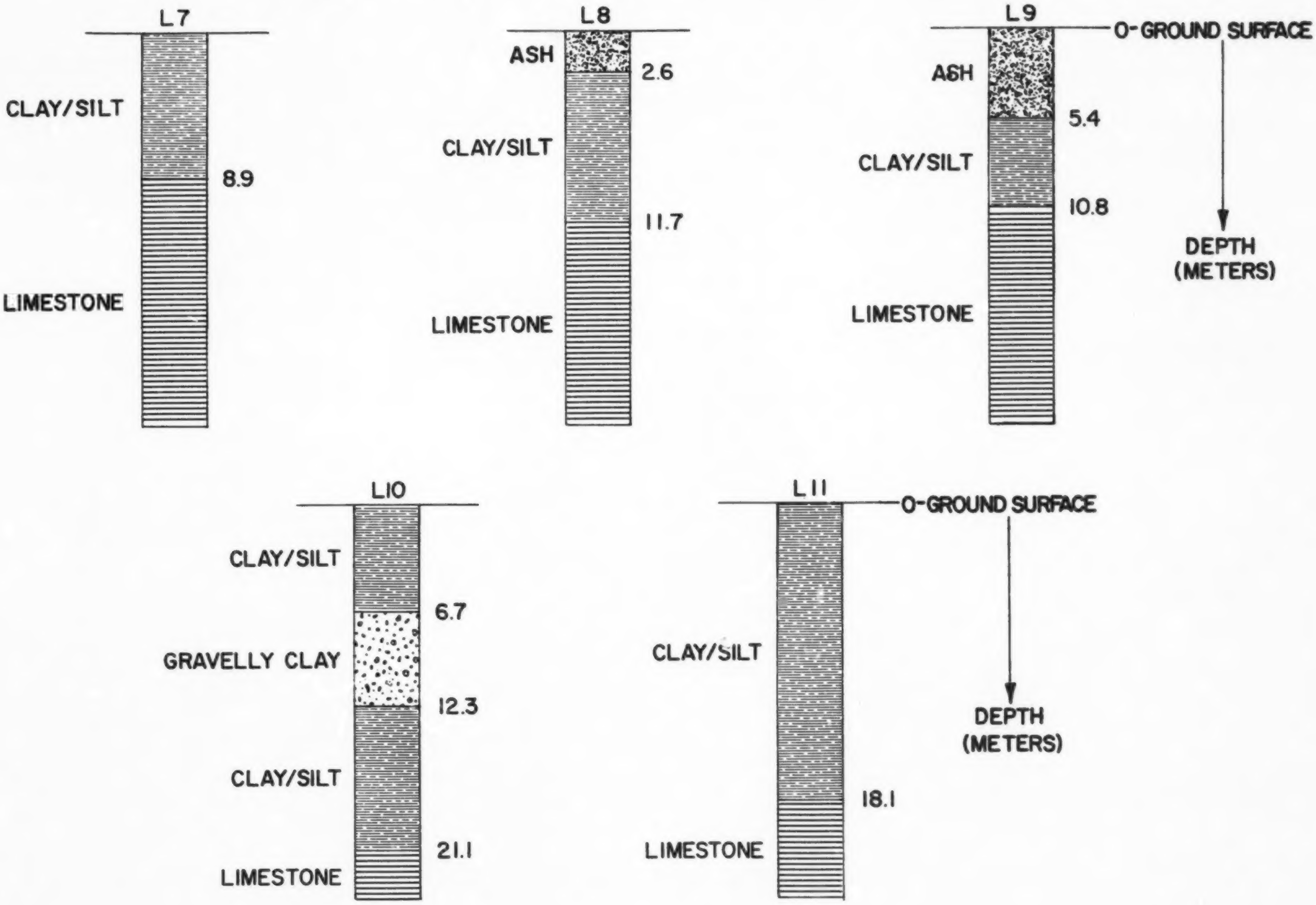
VERTICAL PROFILE OF THE SUBSTRATUM AT PLANT J's MONITORING WELL LOCATIONS


J1
CLAY/SILT
4.1
SHALE
J2
ASH
13.4
CLAY/SILT
16.0
SAND
18.4
SHALE
J3
ASH
9.7
CLAY/SILT
11.1
SAND
15.0
SHALE
J4
0-GROUND SURFACE
CLAY/SILT
8.0
SAND
10.9
SHALE
DEPTH
(METERS)
J5
CLAY/SILT
10.2
SAND
11.8
SHALE
J6
CLAY/SILT
11.4
SAND
14.5
SHALE
J7
CLAY/SILT
8.8
SAND
13.4
SHALE
J8
0-GROUND SURFACE
SHALE
9.3
DEPTH
(METERS)

VERTICAL PROFILE OF THE SUBSTRATUM AT PLANT L's MONITORING WELL LOCATIONS


L1
CLAY/SILT
10.8
LIMESTONE
L2
CLAY/SILT
13.7
LIMESTONE
L3
0-GROUND SURFACE
CLAY/SILT
11.6
GRAVELLY CLAY
13.4
LIMESTONE
DEPTH
(METERS)
L4
CLAY/SILT
9.8
GRAVELLY SAND
14.2
GRAVELLY CLAY
L5
CLAY/SILT
7.8
GRAVELLY SAND
10.8
CLAY/SILT
16.3
LIMESTONE
L6
0-GROUND SURFACE
ASH
10.5
CLAY/SILT
14.4
LIMESTONE
DEPTH
(METERS)

VERTICAL PROFILE OF THE SUBSTRATUM AT PLANT L's MONITORING WELL LOCATIONS


L7
CLAY/SILT
8.9
LIMESTONE
L8
ASH
2.6
CLAY/SILT
11.7
LIMESTONE
L9
0-GROUND SURFACE
ASH
5.4
CLAY/SILT
10.8
LIMESTONE
DEPTH
(METERS)
L10
CLAY/SILT
6.7
GRAVELLY CLAY
12.3
CLAY/SILT
21.1
LIMESTONE
L11
0-GROUND SURFACE
CLAY/SILT
18.1
LIMESTONE
DEPTH
(METERS)

APPENDIX C

ANALYTICAL RESULTS OF COLUMN ATTENUTATION STUDIES

TABLE C-1. ANALYSIS OF COAL ASH LEACHATE USED IN SOIL ATTENUATION STUDY

Constituent	Value	Constituent	Value
pH, std. units	7.8	Lead, mg/l	<0.010
Eh, millivolts	-280	Beryllium, mg/l	<0.002
Temperature, °C	17	Barium, mg/l	0.23
Conductivity, μmhos/cm^2	1800	Manganese, mg/l	4.2
Alkalinity, mg/l as $CaCO_3$	340	Sodium, mg/l	7.2
Calcium, mg/l	185	Potassium, mg/l	14
Magnesium, mg/l	7.6	Selenium, mg/l	<0.002
Iron, mg/l	15	Total dissolved solids, mg/l	720
Copper, mg/l	0.14	Sulfide, mg/l	0.07
Zinc, mg/l	0.04	Sulfate, mg/l	240
Nickel, mg/l	<0.05	Nitrite and Nitrate as nitrogen, mg/l	0.02
Aluminum, mg/l	0.06	Phosphate as Phosphorus, mg/l	0.08
Cadmium, mg/l	<0.01		
Mercury, mg/l	0.002		
Chromium, mg/l	<0.05		

TABLE C-2. ANALYTICAL RESULTS OF COLUMN ATTENUATION STUDIES

	Analysis of effluent from soil column--Plant L						
Composite volume, ml	180	150	180	150	150	180	120
Total volume eluted, ml	180	330	510	660	810	990	1110
Calcium, mg/L	120	180	190	180	180	180	170
Magnesium, mg/L	9.0	9.0	9.3	9.4	9.6	9.6	9.2
Sodium, mg/L	8.6	7.9	8.2	8.1	8.6	8.2	7.9
Potassium, mg/L	6.3	13	14	15	15	14	14
Iron, mg/L	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
Manganese, mg/L	0.48	0.06	0.26	0.44	0.650	0.83	0.86
Copper, mg/L	0.02	0.008	0.007	0.007	<0.005	<0.005	0.007
Zinc, mg/L	<0.05	<0.01	0.19	<0.01	<0.01	0.14	<0.01
Nickel, mg/L	0.18	0.05	0.05	0.09	<0.05	<0.05	0.07
Sulfate, mg/L	300	300	300	240	310	280	270
Cadmium, mg/L	0.009	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
Lead, mg/L	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Chromium, mg/L	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
Aluminum, mg/L	0.09	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Barium, mg/L	0.1	0.08	0.07	0.08	0.1	0.12	0.13
Beryllium, mg/L	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
Mercury, mg/L	0.03	0.0005	0.0003	0.0002	0.0003	0.0003	0.0002
Selenium, mg/L	<0.004	<0.002	<0.002	<0.004	<0.002	<0.002	<0.01

TABLE C-2 (continued)

	Analysis of effluent from soil column--Plant J					
Composite volume, ml	300	270	300	270	300	270
Total volume eluted, ml	300	570	870	1140	1440	1710
Calcium, mg/L	160	160	160	160	160	150
Magnesium, mg/L	10	9.4	9.5	9.5	9.7	9.2
Sodium, mg/L	8.9	8.0	8.0	8.2	8.4	8.2
Potassium, mg/L	10	12	12	13	13	12
Iron, mg/L	0.12	0.068	0.063	0.053	0.039	0.03
Manganese, mg/L	0.5	0.49	0.77	1.1	1.1	0.94
Copper, mg/L	0.02	0.006	0.02	0.006	0.007	0.022
Zinc, mg/L	0.16	0.03	0.02	0.03	0.02	0.02
Nickel, mg/L	1.1	<0.05	<0.05	<0.05	<0.05	<0.05
Sulfate, mg/L	*	*	*	*	*	*
Cadmium, mg/L	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Lead, mg/L	0.032	<0.01	<0.01	<0.01	<0.01	<0.01
Chromium	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
Aluminum, mg/L	0.1	0.05	0.04	0.05	<0.02	0.17
Barium, mg/L	0.12	0.13	0.1	0.16	0.17	0.16
Beryllium, mg/L	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
Mercury	<0.0008	<0.0008	<0.0008	<0.0008	<0.0008	<0.0008
Selenium, mg/L	<0.004	<0.004	<0.004	<0.004	<0.004	<0.004

TABLE C-2 (continued)

	Analysis of effluent from kaolinite clay column						
Composite volume, ml	180	180	180	180	180	180	120
Total volume eluted, ml	180	360	540	720	900	1080	1200
Calcium, mg/L	130	150	150	160	160	170	120
Magnesium, mg/L	9.0	9.9	9.9	9.5	9.2	10	7.2
Sodium, mg/L	9.6	8.5	8.5	8.3	7.8	8.8	7.0
Potassium, mg/L	14	16	16	15	15	16	14
Iron, mg/L	0.046	0.013	0.013	0.022	0.099	0.063	0.014
Manganese, mg/L	0.75	0.22	0.25	0.96	1.1	1.3	0.92
Copper, mg/L	0.045	0.056	0.046	0.039	0.081	0.04	0.16
Zinc, mg/L	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.12
Nickel, mg/L	0.96	0.18	0.07	0.07	0.05	0.05	<0.05
Sulfate, mg/L	*	*	*	*	*	*	*
Cadmium, mg/L	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
Lead, mg/L	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Chromium, mg/L	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
Aluminum, mg/L	0.04	<0.02	<0.02	0.03	0.07	0.06	0.06
Barium, mg/L	0.13	0.15	0.16	0.19	0.17	0.2	0.14
Beryllium, mg/L	<0.0005	<0.0005	<0.0005	<0.0005	<0.0005	<0.0005	<0.0005
Mercury, mg/L	<0.0002	<0.0002	<0.0002	<0.0002	0.0003	0.0003	0.0003
Selenium, mg/L	<0.004	<0.004	<0.004	<0.004	<0.004	<0.004	<0.01

*Not enough sample for analysis.

APPENDIX D

USED IN COLUMN ATTENUATION STUDIES

TABLE D-1. CHEMICAL CHARACTERISTICS OF CLAY MINERALS USED IN COLUMN ATTENUATION STUDIES

Illite

Constituent	Value	Constituent	Value
Chlorine, mg/l	460.0	Zinc, μg/g	17
Sulfate, mg/l	480.0	Nickel, μg/g	26
Bromine	1.2	Cadmium, μg/g	<1.0
Calcium, μg/g	4000	Lead, μg/g	12.0
Magnesium, μg/g	2500	Chromium, μg/g	<5.0
Sodium, μg/g	300	Aluminum, μg/g	7700
Potassium, μg/g	5300	Barium, μg/g	830
Iron, μg/g	6100	Beryllium, μg/g	5.0
Total Manganese, μg/g	65	Mercury, μg/g	0.27
Copper, μg/g	52	Arsenic, μg/g	1.2
		Selenium, μg/g	<1.0

Kaolinite

Constituent	Value	Constituent	Value
Chlorine, mg/l	30.0	Zinc, μg/g	52
Sulfate, mg/l	120.0	Nickel, μg/g	21
Bromine	<0.2	Cadmium, μg/g	<1.0
Calcium, μg/g	120	Lead, μg/g	10.0
Magnesium, μg/g	110	Chromium, μg/g	<5.0
Sodium, μg/g	60	Aluminum, μg/g	840
Potassium, μg/g	70	Barium, μg/g	61
Iron, μg/g	1400	Beryllium, μg/g	3.0
Total Manganese, μg/g	830	Mercury, μg/g	0.60
Copper, μg/g	15	Arsenic, μg/g	10.0
		Selenium, μg/g	<1.0

Montmorillonite

Constituent	Value	Constituent	Value
Chlorine, mg/l	26.0	Zinc, μg/g	70
Sulfate, mg/l	1800.0	Nickel, μg/g	<5.0
Bromine	<0.2	Cadmium, μg/g	<1.0
Calcium, μg/g	770	Lead, μg/g	48.0
Magnesium, μg/g	3400	Chromium, μg/g	<5.0
Sodium, μg/g	1100	Aluminum, μg/g	2900
Potassium, μg/g	200	Barium, μg/g	13
Iron, μg/g	1700	Beryllium, μg/g	2.0
Total Manganese, μg/g	22	Mercury, μg/g	0.17
Copper, μg/g	3	Arsenic, μg/g	2.3
		Selenium, μg/g	<1.0